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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CVIII.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2797.—JULY 4, 1913.

THE RECENT DEVELOPMENT OF NEUTRAL SALT REACTIONS.

By M. FORT.

ALTHOUGH the law of mass action is now of fundamental importance in chemistry, it is frequently neglected or imperfectly appreciated in its bearing on technical and analytical problems, and perhaps is less rarely looked to for an explanation of such than the everyday "common-sense" chemical notions which by constant use, as in routine work, often acquire high false values. Thus one readily thinks of caustic soda expelling ammonia from a salt in solution, but to think of ammonia expelling sodium as sodium hydrate from a sodium salt in solution creates some degree of mental confusion, greater or less according to one's actual familiarity with the potency of mass law.

It became known among chemists (the writer is unaware of the original source) that sodium sulphate and acetic acid, under certain conditions, may react as though free sulphuric acid is actually present. The experiment may be shown with methyl orange as indicator and a hot dilute solution of acetic acid. On adding sodium sulphate a colour change, denoting an increase in acidity, takes place, ascribable to the liberation of a small amount of free sulphuric acid by the action of the weaker acetic acid competing for the base combined in the salt. This reaction was known as the "neutral salt reaction," and was little heard of until recent years. It is a direct outcome of mass law and demands expression by means of a reversible equation :—

$$Na_2SO_4 + 2CH_3\cdot COOH \rightleftharpoons 2NaOOC\cdot CH_3 + H_2SO_4.$$

The equilibrium is determined mainly thus $\leftarrow$, but it is never completed, hence the necessity for the presence of a small amount of free mineral acid, liberated by the weaker organic acid from the neutral salt in attaining equilibrium. As might be expected there is no need for the amount of free acetic to be large in order to get an appreciable amount of sulphuric acid formed, if the mass of sodium sulphate present be considerable. The reaction is favoured by rise in temperature, as this increases the extent of hydrolytic dissociation of the neutral salt, which dissociation is supposedly necessary before the neutral salt reaction can take place.

A further observation was made by L. L. Lloyd (*Journ. Soc. Chem. Indus.*, 1910, p. 1361), namely, that in a neutral salt reaction between formic acid and sodium sulphate, the presence of wool greatly increases the amount of sulphuric acid formed, in fact from a mere trace to a distinctly appreciable amount. Lloyd obtained some of the free acid from the wool by extraction with water. This is the first indication of the recognition of the important influence exerted by neutral salt reactions in technical chemistry.

Quite apart apparently from this work is an observation of Arndt's (*Zeit. Anorg. Chem.*, xxviii., 365), that by heating a strong solution of sodium sulphate with litmus an alkaline reaction is obtained. This was confirmed by Kraus (*Farb. Zeit.*, 1911, p. 333), and applied by him to explain certain phenomena connected with the dyeing of wool, *e.g.*, the deterioration of the wool fibre dyed in so-called neutral dye-baths with sodium sulphate as assistant. He could not, however, obtain similar alkalinity with sodium chloride, and Dreaper (*Journ. Soc. Dyers and Co.*, 1911, p. 293) suggested that the difference lay in the inability of sodium chloride to react in a similar way to the following :—

$$Na_2SO_4 + H_2O \rightleftharpoons NaOH + NaHSO_4.$$

Later work has explained these observations in a more satisfactory way.

It appeared to the author that the known neutral salt reaction if correctly understood must have a counterpart in the reactions of weak bases with salts of stronger bases, and considerable evidence was acquired of such being the case (Fort, *Journ. Soc. Dyers*, 1912, p. 314). In the first place Arndt's observation was confirmed, using also alizarin as indicator, and a series of salts classified on the basis of alkalinity or the absence of an alkaline reaction at the boil. Later it was shown by the author, after extending his knowledge of neutral salt reactions, that the supposed alkalinity of sodium sulphate at the boil is not due to special conditions of ionisation determined by rise in temperature, as was tentatively suggested by Procter (*Journ. Soc. Dyers*, 1913, p. 40), but is part of a neutral salt reaction with the acidic indicator, *e.g.*, in the case of alizarin a small quantity of coloured sodium alizarate is formed, and a similar explanation covers the reaction with litmus. On cooling the colour disappears, due to a reversal of the reaction. Since sodium chloride is the salt of a stronger acid than sodium sulphate it is not so readily hydrolysed and decomposed by alizarin, and hence shows no colour reaction at the boil. However, by using a more strongly acid indicator, for example di-nitro-anthrachrysone-di-sulphonic acid, a distinct alkaline colour reaction was obtained with sodium chloride at the boil. Further, it was shown that by using as indicator a drop or two of a dilute solution of rosaniline base carefully decolorised with very dilute caustic soda, on heating with a solution of sodium chloride or sulphate a pronounced magenta colour appeared, *i.e.*, an acid reaction was given. In fact there is no evidence of the supposed alkalinity of sodium sulphate solution at the boil, apart from a neutral salt re-

action with the indicator used, which agrees with the apparently surprising fact that the same sample of sodium sulphate may be made to show either an acid or an alkaline colour reaction in hot solution according to whether the indicator be respectively basic or acid in character. In this type of reaction the presence of water is regarded as essential to give hydrolytic dissociation of the salt which is increased greatly as temperature rises, with the result that the free weak acid or base can compete for base or acid respectively as the case may be, formed from the salt by hydrolysis, thereby causing the formation of more or less of the free strong acid or base from the salt. The former phase of the reaction is seen in the colour indications obtained from sodium sulphate as described above.

The latter phase of the neutral salt reaction, *i.e.*, the liberation of varying small quantities of strong acids or bases by the interaction of solutions of their salts with weaker acids or bases, is of great technical interest.

A new neutral salt reaction was described by the author (1912, *loc. cit.*), who found that on adding sodium sulphate or chloride to a boiling aqueous solution of aniline in a platinum dish, containing alizarin as indicator, an alkaline colour reaction was obtained at once. This is assumed to be due to two reactions :—

$$\text{(i.)}\ NaCl + H_2O \rightleftarrows NaOH + HCl.$$

$$\text{(ii.)}\ C_6H_5{\cdot}NH_2 + HCl \rightleftarrows C_6H_5{\cdot}NH_2{\cdot}HCl.$$

Similar reactions were obtained with a variety of organic bases, and also one found it possible to show even the ability of ammonia to release caustic soda in a solution of a neutral sodium salt. Phenolphthalein was used as indicator, and as is well known it reacts feebly and incompletely with ammonia in dilute solution; in fact the pink colour obtained in the cold fades on warming, due presumably to increased hydrolysis of the rather unstable coloured compound as temperature rises. The same influence, however, promotes the neutral salt reaction, as was explained previously. If, then, a dilute solution of ammonia be taken of such a strength as to give a faint pink colour with phenolphthalein at the boil, on adding sodium sulphate or sodium chloride to the hot solution a much deeper pink is at once shown. The experiment may be varied by starting with two portions of cold dilute ammonia just strong enough to give a colour with phenolphthalein, to one portion sodium chloride being added before gently heating. The portion containing the neutral salt may be shown to remain pink up to the boil, while the other fades on warming through a few degrees. On cooling a similar shade is regained in each case.

The author has been led to believe also in another type of reaction, *i.e.*, the double neutral salt reaction which must take place in solution, between any two neutral salts obtained from different acids and bases, resulting in the establishment of an equilibrium in which all four possible salts of these acids and bases are concerned. For example, it is found that neither calcium sulphate nor sodium chloride give a colour reaction when a solution is boiled with alizarin as indicator, the contrary being the case with sodium sulphate, as was mentioned. However, by adding sodium chloride to a boiling solution of calcium sulphate in a platinum dish, the crimson alkaline reaction with alizarin is obtained. This is explained as due to an equilibrium involving the formation of appreciable quantities of calcium chloride and sodium sulphate, sufficient to give the above colour reaction.

Technical and other Applications.

There has been rapid application of the knowledge of these reactions to industrial problems. Procter has applied it to the pickling of hides (*Collegium*, 1912, No. 512, p. 687), and has shown that N/10 formic acid along with common salt can fix in gelatin an amount of hydrochloric acid equal to that taken up from N/10 hydrochloric acid itself. L. L. Lloyd has also adequately explained the formation and avoidance of salt stains on hides by means of neutral salt reactions (*Collegium*, 1913, No. 517, p. 188), and also the occurrence of tendered cotton threads in half wool unions after dyeing in a bath containing as assistants formic acid and Glauber's salt. This latter instance may be used to show how the knowledge recently acquired may solve very troublesome technical difficulties. It was well established and accepted that formic acid does not tender cotton, and it found favour with dyers largely on account of this great advantage which it possesses over sulphuric acid. It is a matter of equal faith that sodium sulphate alone causes no deterioration of the cotton fibre, and apparently no one saw any reason why danger should be apprehended when these assistants were used together; indeed, although occasional tendering of batches of goods occurred where it was most difficult to avoid the correct or something approaching the right conclusion, the "common-sense" view of the impossibility of a weak acid like formic setting free sulphuric acid, seems to have prevented its being reached. Lloyd showed that not only is sulphuric acid produced, but being absorbed by the wool present the reaction is much more considerable, and free sulphuric acid can be extracted from the fabric with water in appreciable amount. By a thorough rinsing after dyeing, troubles from this cause may be largely obviated.

The author has shown that wool itself can to some extent decompose even such stable salts as sodium sulphate in boiling baths, both the strongly basic and apparently weaker acid properties of the amphoteric fibre-substance being involved (*Journ. Soc. Dyers*, 1913, p. 80). The basic properties of wool are no doubt mainly responsible by causing the transference of sulphuric acid to the fibre, while the prevailing acidity of a portion of the wool or its hydrolysis products causes a part of the fibre to be dissolved away by the alkali constituent of the salt. This is the reason for the injury done to the lustre of wool when dyed in hot neutral baths containing Glauber's salt, which may be largely avoided by addition of glue to the dye bath. As may be well understood from what has been said, common salt is injurious to a less degree and is often preferred, *e.g.*, by garment dyers, on that account. Further, it was shown that a certain degree of tendering of cotton in a half-wool union fabric may be caused by a hot bath of sodium sulphate in the following way :—The wool combines with sulphuric acid obtained from the salt, as already explained, and retains a portion firmly in spite of washing with water, which on drying and storing is partly set free, in which state it tenders the cotton fibres present (*Journ. Soc. Dyers*, 1913, p. 120).

Very recently Lloyd has explained to the Society of Dyers and Colourists (London Section) the causes of certain defects in silk fabrics. Silk is found to decompose to some extent mineral halides in solution, forming halogen compounds with the silk fibre, from which later the free halogen may be liberated and give rise to oxidation and deterioration of the fibre on keeping.

The recent legislation against filthy flock for upholstery purposes has set up a minimum chlorine content as a standard of purity, which, however, it is found may be approached by fresh clean wool (*Journ. Soc. Chem. Ind.*, 1913, p. 402), a discovery which, in the light of what has been said, may be accounted for by conditions on the live sheep, *i.e.*, the presence of organic acids and mineral chlorides from perspiration. The ordinary perspiration test applied to dyed fabrics is a treatment with weak acetic acid, and has proved to be quite inadequate for practical conclusions to be drawn. The author has for some time replaced this test in his own laboratory by a test employing common salt in conjunction with acetic acid, and may now recommend it for use where the ideal one of actual wear is inapplicable. A similar modification for the purposes of an alkaline perspiration test might be arranged, *e.g.*, for horse cloths.

The physiological interest attached to the neutral salt reactions is necessarily great, but at the present one may

not dogmatise much. However, it is clear *à priori*, for example, that organic acids of the stomach or fruit acids in presence of common salt or mineral chlorides taken with food, will set up an equilibrium in which free hydrochloric acid will play a part, and in which albuminoids also present can favour the production of this mineral acid (compare the effect of hide, wool, and silk substance in this connection), which being required for digestion of these same albuminoids, will be produced as required in complete accordance with beneficent natural law. In regard to the known secretion of hydrochloric acid from special glands, as distinct from its formation by reactions among the contents of the stomach, the amount of sodium chloride in the blood forming a permanent reserve may be looked to as the starting material, and a neutral salt reaction as the most likely chemical means to be employed. The author has not been afforded opportunity of an experimental justification of this view, as was originally intended, owing to a greater personal interest in the rapidly developing textile applications of the knowledge of neutral salt reactions. This knowledge has suggested an explanation of a root difficulty in the acceptance of the chemical theory of dyeing, namely, as to how a free colour acid, the dyeing of which on wool is greatly promoted by a previous treatment of the fibre with sulphuric acid, can effect combination with wool already combined with a strong acid. In the author's opinion the first part of the answer to this is that the partial hydrolysis of the wool by the acid causes a great increase in the available basic parts of wool, and secondly, that local conditions in or on the fibre favour a reaction offering great analogy with neutral salt reactions, for it is found that wool, after treatment with sulphuric acid and then with water till no more acid is removed by extraction, will readily absorb free colour acids, *e.g.*, picric acid and certain azo-sulphonic acids, at the same time liberating an appreciable amount of free sulphuric acid, not necessarily equivalent in amount but at any rate somewhat similar. Fuller evidence acquired in this matter will be published at an early date.

These are the main features of the development of the knowledge of neutral salt reactions, and of its ready application to a diversity of subjects, and in the latter connection considerable progress may still be looked for.

Technical College, Bradford.

REFORM OF CHEMICAL CALCULATIONS.

By C. J. T. HANSSEN.

In Chemical News, November 1, 1912 (vol. cvi,, p. 215) are collected from the last fifteen years atomic weights given in plain figures, and there arranged into a kind of atomic weight table; the author has now extended this list to 76 elements, and respectfully invites chemists to investigate this table, which, if proved and accepted, would very much simplify chemical calculations and operations.

International Atomic Weights, 1913.

1.	Hydrogen	H	1
2.	Helium	He	4
3.	Lithium	Li	7
4.	Glucinium	Gl	9
5.	Boron	B	11
6.	Carbon	C	12
7.	Nitrogen	N	14
8.	Oxygen	O	16
9.	Fluorine	F	19
10.	Neon	Ne	20
11.	Sodium	Na	23
12.	Magnesium	Mg	24
13.	Aluminium	Al	27
14.	Phosphorus	P	31
15.	Sulphur	S	32
16.	Chlorine (35·46)	Cl	?
17.	Potassium (39·10)	K	?
18.	Calcium	Ca	40
19.	Scandium	Sc	44
20.	Titanium (48·1)	Ti	?
21.	Vanadium	V	51
22.	Chromium	Cr	53
23.	Manganese	Mn	55
24.	Iron	Fe	56
25.	Nickel (58·68)	Ni	?
26.	Cobalt	Co	59
27.	Copper (61·57)	C	?
28.	Zinc (65·37)	Zn	?
29.	Gallium	Ga	70
30.	Germanium (72·5)	Ge	?
31.	Arsenic	As	75
32.	Selenium	Se	79
33.	Bromine	Br	80
34.	Krypton (82·9)	Kr	?
35.	Rubidium (85·7)	Rb	?
36.	Strontium (87·6)	Sr	?
37.	Yttrium	Yt	89
38.	Zirconium (90·6)	Zr	?
39.	Columbium	Cb	94
40.	Molybdenum	Mo	96
41.	Ruthenium	Ru	102
42.	Rhodium	Rh	103
43.	Palladium	Pd	107
44.	Silver	Ag	108
45.	Cadmium	Cd	112
46.	Tin	Sn	119
47.	Antimony	Sb	120
48.	Iodine	Io	127
49.	Xenon	Xe	128
50.	Cæsium	Cs	133
51.	Barium (137·7)	Ba	?
52.	Lanthanum	La	139
53.	Cerium	Ce	140
54.	Neodymium (144·6)	Nd	?
55.	Samarium	Sa	150
56.	Europium	Eu	152
57.	Gadolinium	Gd	156
58.	Terbium	Tb	160
59.	Dysprosium (162·5)	Dy	?
60.	Erbium	Er	166
61.	Thulium	Tm	171
62.	Ytterbium	Yb	173
63.	Lutecium	Lu	174
64.	Tantalum	Ta	181
65.	Tungsten	Wo	184
66.	Osmium	Os	191
67.	Iridium	Ir	193
68.	Platinium	Pt	195
69.	Gold	Au	197
70.	Mercury	Hg	200
71.	Thallium	Tl	204
72.	Lead	Pb	207
73.	Bismuth	Bi	208
74.	Radium	Ra	225
75.	Thorium	Th	233
76.	Uranium	U	240

Copenhagen, Valdemarsgade 3.
June 23, 1913.

Synthesis of Borides in Vacuum Furnace.—E. Wedekind.—The electric vacuum furnace can be used to effect syntheses of simple compounds of metals of high melting-point provided that the mixture is pressed into rods and these conduct the current sufficiently. This condition is fulfilled with mixtures of many metals with boron and the following borides have been prepared thus:—Zirconium boride, Zr_3B_4; vanadium boride, VB; uranium boride, UB_2. Experiments with molybdenum and titanium were failures.—*Berichte*, xlvi., No. 5.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

New Method to Foretell the Weather: The Guilbert Method (Hitherto Unpublished).

For the last few years a new method for forecasting the weather, the Guilbert method, has daily been enregistering new successes. Scientific men, such as Prof. Bernard Brunher, formerly Director of the Puy-de-Dôme Observatory, M. Violle, the learned physician, member of the French Institute, and the late Tersserenc de Bort, already very justly appreciated the meteorologist Gabriel Guilbert.

Violently controverted by the Control Meteorological Bureau of France, M. Guilbert has, however, received numerous encouragements from abroad. At Hamburg, at Valencia in Spain, at Belt in Holland, and also in Portugal, the meteorological observatories use his method of foretelling the weather.

In what does this method consist? M. Guilbert himself thus explains it to us:—The method of foretelling the weather at short spaces of time, known under the name of the Guilbert weather, is simply based on observation. M. Guilbert believes that the wind on the surface of the globe is the *cause*, at least apparent, of barometrical variations at twenty-four hours distance. So then, according to him, there is a relation of cause and effect between the speed and the direction of *superficial* winds and the consecutive variation of the pressure. Hence it is easy to conceive all the importance of this relation, if we consider that weather, in the widest sense of the word, depends, theoretically, on barometric pressure, and especially on the respective disposition of the centres of high and low pressure.

The essential aim of the method is precisely the prevision of forecast of these oscillations of pressure, to arrive at which it employs a certain number of rules. The method is, however, extremely simple, in this sense, that it requires only one single observation, that of the wind, the easiest of all, but over vast extents as over a large part of Europe for example. This method eliminates all other indications; it does not take into consideration the thermometrical or hygrometrical variations, the zones of rain or of fine weather; it leaves aside the winds of mountains and high regions as well as the atmospherical calorific or magnetic observations. Of all the elements generally considered in daily forecasts of the weather this method utilises only the *wind* and the variation of pressure.

But if the fundamental basis of the method is thus very simple, the application of the rules is more complicated and requires a veritable study. At the outset it is necessary to discern the different relative or absolute speeds of the surface winds, so as to discover the winds that the method designates as normal and abnormal, as convergent and divergent.

According to classical teaching, the wind is proportional to the gradient, that is to say, to the atmospherical slope, to the declivity of the air, so to say, compared with the declivity of the ground. The greater the importance of the slope, that is to say of the gradient, so much the more does the wind acquire speed. Now, M. Guilbert has remarked that on many days this notion was inexact. With a steep gradient, the wind remained weak, and inversely blew with force when the gradient was but weak.

It is from this observation M. Guilbert has deduced the fundamental principle of his method: the principle of *normal wind*. Normal wind is merely wind proportional to the gradient; abnormal wind will be so *by excess* if the wind is stronger than the gradient allows for theoretically, they will be abnormal by default if they are too weak. Now, winds abnormal *by excess* determine a barometrical rise, generally proportional to the abnormality observed in the twenty-four hours. Inversely the winds abnormal *by default* determine a fall of the barometer. Now a determining of these mere movements of barometric pressure allows the forecast of the future of squalls, and also makes it possible to know if such or such depression will be filled up or hollowed out, and if consequently the wind is going to increase or decrease. In certain circumstances, when the abnormal winds *by excess* surround a centre of depression, this centre is completely destroyed: tempestuous winds sometimes—and thus the method foretells—are followed by a perfect calm in a delay of twenty-four hours, sometimes even in twelve hours. It is the phenomenon called in the Guilbert method by the name of "Compression of the Cyclone."

The distinction of the winds designated as convergent and divergent is not less important. The former have a tendency to contract the depression, to push it back, they constitute a resistance of the invading march of the cyclone or tend to destroy it; the latter, on the contrary, are attractive winds; they constitute centres of attraction of less resistance: they determine the fall of the barometer and sometimes even create a hurricane.

Wind, both generator of tempests and calms; wind considered as the only regulator of atmospheric pressure tending ceaselessly to level if it is possible to thus express the idea—the aerial layers, such is the directing hypothesis of the Guilbert method.

The large proportion of successes obtained in the forecasts of the weather according to the above related principles shows incontestably that this point is the result of mechanical effects due to the mere action of the surface winds.

A Disease of Metals.

The first contagious disease of metals was discovered several years ago, by some chemists, on tin. The disease of tin is now well known. Prof. Hanriot, Director of the Metal Tests at the French Mint, has just recently discovered a new disease with which alloys may be afflicted. The alloy (copper-aluminium), containing 97 per cent of aluminium and 3 per cent of copper, which hardens the former of the two metals, is employed especially in the manufacture of helmets and other military objects and utensils. Now, in the Government stores and depôts, especially at Orleans, it has just lately been observed that thousands of copper-aluminium utensils are afflicted with this epidemic disease, which spreads from one object to another, corroding the metal and making holes in it. As the French War Department possesses about 25 to 30 millions worth of francs of objects manufactured with this alloy, measures have been taken to discover the origin of the evil. MM. Hanriot and Le Chatelier, the learned chemist of the Academy of Sciences, have been asked to elucidate the problem.

According to M. Chatelier the origin of the disease is due to a defect in the cold-hammering, but this opinion did not resist the experiments of M. Hanriot, who noticed that the copper-aluminium alloy was not stable. In certain conditions a veritable *migration of the copper* takes place. The copper emigrates to form, with the aluminium, a bronze of aluminium (50 per cent of aluminium and 50 per cent of copper), which is a stable alloy. But by this emigration there are formed on the surface of the metal holes with sides sometimes as long as 2 centimetres.

This disease spreads by contact, and the metal suffering from it looks as if it were attacked by eczema. A light grey spot appears at irregular intervals. The object may then be considered as lost and done for, as up till the present time no remedy is known for this singular affection.

A New Stereoscope.

When you look into an ordinary stereoscope there is a dissociation between the convergence which is preserved and the accommodation which is suppressed, by reason of the presence of the eye-glasses. Moreover, these latter and their mountings are a little joined to the effect produced, and the eyes cannot manage to get entirely free from them. Then, again, stereoscopic images are always small, and it is only, thanks to the enlargement by the

lenses of the eye-glasses, that the objects are seen at their real angle, so that the vision through a stereoscope is, as it were, a vision seen through a magnifying glass. For all these reasons the vision through a stereoscope differs sensibly from the normal vision. M. André Cheron, in a notice sent to the Academy of Sciences by Prof. Lipmann, shows that he has managed to construct a stereoscope whose aim is in a certain measure, as far as possible, to correct these inconveniences. The two pictures are projected on to one plane by two objectives of the same focus. Moreover, the two images are concentred and superposed on their plane of projection, thanks to the presence of an achromatic lens covering the two objectives projecting the images. On the plane of the formation of the images is a condensor, which makes the rays coming from the right picture converge towards the right eye, and those proceeding from the left picture towards the left eye. In this way the spectroscopic relief is integrally preserved and the eyes converge and accommodate themselves as if they were looking at objects really situated in space. The pictures are enlarged and looked at at the distance of distinct vision, without anything being interposed between them and the eyes of the observer.

The Contamination of Milk.

We all know how easily milk is contaminated. MM. Trillat and Fouassier, of the Paris Pasteur Institute, in a work on the frequency of the contamination of fresh milk by water containing infinitesimal quantities of typhoid bacilli, have recognised that the contamination might also take place even with water which from a bacteriological analysis might be declared healthy and sound. The typhoid bacillus is unperceived during the first hours of contamination. The development of the culture then takes place quickly, as it were, like an explosion.

MM. Trillat and Fouassier establish the fact that in its turn milk may become a frequent cause of the contamination of water in many circumstances, and this observation brings out clearly the reciprocal influence of water and of milk for their mutual typhoid fertilisation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*Atomic Specific Heats between the Boiling-points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Absolute of the Elements a Periodic Function of the Atomic Weights.*" By Prof. Sir James Dewar, F.R.S.

"*Active Modification of Nitrogen Produced by the Electric Discharge.*" (V.). By Hon. R. J. Strutt, F.R.S.

1. An improved practical method of preparing and storing nitrogen for the experiments is described.

2. It is shown, notwithstanding criticisms of certain other experimenters, that the presence of traces of oxygen in the nitrogen used is not essential, or even favourable, to the phenomena. The nitrogen used, purified by cold phosphorus, does not contain oxygen to the extent of 1 part in 100,000. Passing it over red-hot copper in addition makes no difference. The intentional addition of oxygen does harm; 2 per cent obliterates the effects altogether. Hydrogen and carbon dioxide as impurities are much less harmful, but traces even of water vapour have a very bad effect.

3. Nitrides are formed by the admixture of active nitrogen with vapour of mercury, cadmium, zinc, arsenic, sodium, and sulphur. These are decomposable by water or potash solution, yielding ammonia.

4. Carbon disulphide yields a blue polymeric nitrogen sulphide, and polymeric carbon monosulphide. Chloride of sulphur gives ordinary yellow nitrogen sulphide. Stannic chloride and titanium tetrachloride also yield solid products. In the latter case nitrogen was proved to be present.

5. All organic compounds tried, except carbon tetrachloride, yield hydrocyanic acid freely, but not cyanogen, as was proved by chemical tests. When chlorine is present, cyanogen chloride is formed. Benzene yields (almost certainly) cyanobenzene.

6. The intensity of the cyanogen spectrum with organic compounds is no index of the quantity of hydrocyanic acid being formed. Preponderance of the red cyanogen bands is associated with cyanogen chloride or bromide.

On a general view of the evidence, there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress.

"*Electrical Emissivity and Disintegration of Hot Metals.*" By Dr. J. A. Harker, F.R.S., and Dr. G. W. C. Kaye.

Preliminary experiments have been carried out on the volatilisation and electrical emissivity of a number of metals, mostly in nitrogen at reduced pressures. The metals were heated by alternating current and no applied potential was employed.

1. The emission of positive electricity occurs at temperatures from about 1000° to 1400° C. For metals which melt within this range, a sudden and marked increase in the positive current often occurred at the liquefying point —due, probably, to the sudden release of occluded gas.

2. Oxygen appears to augment the positive current.

3. At higher temperatures, negative electricity predominates and increases rapidly with the temperature. The negative current attained with iridium at the melting-point was 80 milliampères, with tantalum at 1670° C. 220 microampères, with iron at the melting-point 90 microampères. In the case of carbon in air at atmospheric pressure, an ionisation current of 3½ ampères was obtained.

4. The negative current at moderate pressures appears to be largely increased if the conditions are such that considerable sputtering of the metal occurs.

5. The negative currents are probably a consequence of chemical reaction between the metal and the surrounding gas.

6. Carbon becomes plastic in the neighbourhood of 2500° C. At such temperatures it also readily sublimes.

"*Method of Measuring the Viscosity of the Vapours of Volatile Liquids, with an Application to Bromine.*" By A. O. Rankine, D.Sc.

In this method of determining viscosities the rate of transpiration of the vapour through a capillary tube is controlled by the vapour pressures of the liquid itself, a difference of pressure being established in the process of virtually distilling the liquid through the capillary.

The pressures can be estimated without the use of mercury gauges—a state of affairs especially desirable in the case of the halogens.

The viscosities of unsaturated bromine vapour over the approximate range 10° C. to 250° C. have been measured, and, except at the lowest temperatures, are found to agree well with Sutherland's formula, notwithstanding the fact that all the temperatures are below the critical.

The constancy of the proportion $\eta c^{\frac{1}{3}}/A$ (ηc = viscosity at critical temperature; A = atomic weight), as compared with chlorine, has been tested, and the agreement is good.

"*Efficiency of Selenium as a Detector of Light.*" By E. E. Fournier d'Albe.

The efficiency of a selenium preparation used as a detector of light is defined as the amount of additional conductivity imparted to it by the unit of incident light. It is best stated in "micro-ohms" per lumen. Since many factors affect the efficiency of a given selenium bridge, standard conditions are chosen, chief among them being an illumination of one lux. The law of light action is

studied, and the total effect is shown to be proportional to the square root of the incident energy, while the instantaneous effect is proportional to the energy. This is verified down to an illumination of 0·00001 metre-candle. It is shown that selenium is the most efficient light detector known, that it is capable of discriminating minute differences of luminous intensity far beyond the capacity of the eye, and that, with suitable means of detecting minute currents, it should offer a means of testing the quanta theory of light by direct experiment.

"*The Hall Effect in Liquid Electrolytes.*" By A. E. Oxley.

Experiments have been made on aqueous solutions of copper sulphate, silver nitrate, cadmium sulphate, and on copper sulphate gel. Each substance was placed in a small cell of glass or mica, and was subjected to a uniform magnetic field. A Paschen galvanometer was used to measure the transverse potential difference. In a uniform magnetic field this transverse potential difference is due partly to a true Hall effect (depending on the difference of the ionic mobilities) and partly to a concentration Hall effect (depending on the sum of the ionic mobilities). The latter effect is primarily the one which has been measured in this research, and the former, which is smaller, is included. Eight experiments have been made, and the transverse potential differences, which changed sign on reversal of the magnetic field, have been found to agree with the calculated values. The relation between the transverse potential difference and the intensity of the magnetic field, for an aqueous solution of copper sulphate, is linear.

"*Displacements of the Particles and their Paths in some Cases of Two-dimensional Motion of a Frictionless Liquid.*" By Prof. W. B. Morton.

"*Diurnal Variations of the Earth's Magnetism produced by the Moon and Sun.*" By S. Chapman.

"*Electric Effect of Rotating a Magnetic Insulator in a Magnetic Field.*" By Prof. H. A. Wilson, F.R.S., and Marjorie Wilson.

"*Magnetic Materials in Claywares.*" By Arthur Hopwood.

The author has found that white, cream, grey, yellow, buff, red, or brown claywares are feebly or moderately magnetic owing to the presence of unfused grains of unchanged ferruginous minerals and fused globules of complex ferruginous silicates; while flashed, brindled, or blue claywares are always strongly magnetic owing to the presence of complex ferruginous silicate and finely disseminated magnetic oxide of iron.

The origin of the complex ferruginous silicates in claywares is quite different from that of the magnetic oxide of iron. While the latter is produced either by the orientation of the magnetite, originally present in the clays, or by the reducing action of the kiln gases on the precipitated or colloid oxides, hydroxides, or carbonates of iron disseminated throughout the clays, the former are produced by the fusion of the granular or concretionary ferruginous minerals, *i.e.*, iron pyrites, siderite, hæmatite, magnetite, biotite, &c., occurring in the clays with the surrounding matrix. When clays are heated in strongly oxidising kilns ranging in temperature from 600° to 1000° C. they become magnetic owing to the orientation of unchanged magnetic minerals, and when heated in strongly oxidising kilns ranging in temperature from 1000° to 1350° C. they become magnetic, partly owing to the orientation of unchanged magnetic minerals and partly to the conversion of granular or ferruginous minerals to complex ferruginous silicates; but when clays are heated in reducing kilns ranging in temperature from 600° to 1350° C. they become magnetic owing to the formation of complex ferruginous silicates and magnetic oxide of iron.

The amounts of the magnetic materials present in the different sorts of claywares made in various parts of the country show that great care must be exercised in the selection of the materials for the construction of physical laboratories and magnetic observatories, or serious disturbances may take place during observations with delicate magnetic instruments.

"*Synthesis of the Anhydrides of α-Aminoacyl Glucosamines.*" By Arthur Hopwood and Charles Weizmann.

"*Flexure of Telescope Mirror Discs arising from their Weight, and its Influence upon Resolving Power.*" By H. S. Jones.

"*On Fourier Series and Functions of Bounded Variation.*" By Prof. W. H. Young, F.R.S.

"*Condition that a Trigonometrical Series should have a certain Form.*" By Prof. W. H. Young, F.R.S.

"*Trigonometrical Series whose Cesaro Partial Summations Oscillate Finitely.*" By Prof. W. H. Young, F.R.S.

CHEMICAL SOCIETY.

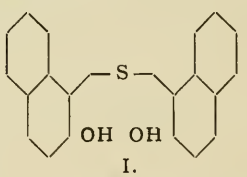
Ordinary Meeting, June 5th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

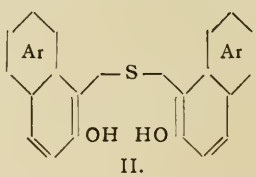
(Concluded from vol. cvii., p. 311).

184. "*β-Naphthol Sulphide and* iso-*β-Naphthol Sulphide; and the Constitution of β-Naphthol.*" By Thomas Joseph Nolan and Samuel Smiles.

The results of previous experiments were used in discussing the constitution of the two sulphides. It was concluded that the normal sulphide is the true *α*-sulphide of *β*-naphthol (I.), whilst the *iso*sulphide, which is formed by reducing naphthasulphonium-quinone, is represented as in II., and may be regarded as the hydrosulphonium-quinone:—



I.



II.

The constitution of *β*-naphthol was also discussed, and it was concluded that in this substance, and probably also in naphthalene, the hydrocarbon nucleus exists in a symmetrical condition.

185. "*Nitrites of Thallium, Lithium, Cæsium, and Rubidium.*" By Walter Craven Ball and Harold Helling Abram.

Thallous nitrite, $TlNO_2$, is a bright orange-red soluble crystalline salt.

Hydrated lithium nitrite crystallises with 1 molecule of water, as stated by Rây (*Proc.*, 1908, xxiv., 75).

Cæsium nitrite, previously examined by Jamieson (*Am. Chem. Journ.*, 1907, xxxviii., 616) closely resembles the potassium salt, as also does rubidium nitrite.

186. "*Note on the Fat of the Seeds of* Oncoba echinata; *Occurrence of Chaulmoogric Acid.* By Ernest Goulding and Noel Charles Akers.

Samples of the seeds of the "Gorli" plant (*Oncoba echinata*, Oliver) have been received at the Imperial Institute from Sierra Leone, and have been examined with the following results.

The seeds contained 5·8 per cent of moisture, and, on extraction with light petroleum, yielded about 47 per cent of a hard opaque white fat of a crystalline appearance and possessing a peculiar characteristic odour. The fat furnished the following constants: D100°/15·5° 0·898, $[\alpha]_D$/17 +48·8°; acid value, 4·5; saponification value, 192·4; iodine value, 99·7; Hehner value, 96·5; Reichert-Meissl value, nil; unsaponifiable matter, 1·5 per cent. It

had no definite melting-point, but gradually liquefied above 35°, and was completely melted at 45°.

The fatty acids obtained by hydrolysing the fat had an iodine value of 105·1, $[\alpha]_D/18$ +52·5°, and consisted of a mixture of a crystalline solid and a liquid. By pressing the mixture between folds of filter-paper, a large proportion of the solid substance could be separated, and on re-crystallisation from warm alcohol it was obtained in thin lustrous plates, melting at 69°. This acid gave an iodine value of 90·5, and $[\alpha]_D/17$ +60·0°; it was identified as chaulmoogric acid, $C_{17}H_{31}\cdot CO_2H$ (Power and Gornall, *Trans.*, 1904, lxxxv., 846), by the analysis of the silver salt and the preparation of the methyl ester, which melted at 22°, and had $[\alpha]_D/21$ +55·8°.

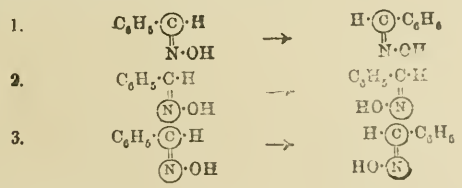
The liquid portion of the fatty acids, although saturated with chaulmoogric acid, gave an iodine value of 122, showing that the liquid acids are highly unsaturated; it darkened rapidly on exposure to the air.

The investigation showed that the fatty acids consisted approximately of chaulmoogric acid, 87·5 per cent, and liquid acids, 12·5 per cent.

187. "*A New Model to Illustrate the Walden Inversion.*" By William Edward Garner.

This model consists of a wooden ball, divided vertically into three equal sections, which are bolted together so as to leave a space between each. Additional stability is conferred on the structure by rings situated at the top and the bottom of the model. To each of the bolts, which are placed as near the centre of the model as possible, is attached a steel arm, capable of being vibrated with an upward and downward motion. The three arms are connected by thin cord to the middle of a central glass or metal rod DD′, which passes through the two rings. The method of attachment is seen by reference to the diagram (Fig. 2). By the movement of the central rod upwards through the rings, the three arms are caused to move simultaneously, and if this movement is made sufficiently great, they pass downwards into the enantiomorphous position.

The Werner model, constructed by the author (*Proc.*, 1912, xxviii., 65), was utilised to illustrate the change of maleic acid into fumaric acid, without the destruction of the double bond, and its employment in this connection naturally suggested its use in the transformation of *syn*- into *anti*-oximes. In the latter case the inter conversion of the isomeride may be demonstrated in either of two ways, namely, (1) by the inversion of the valencies of the carbon atom, and (2) by the inversion of those of the nitrogen atom. If both the carbon and nitrogen atoms undergo inversion, no change in the oxime is produced. The three cases are illustrated below:—



The first method was easily carried out by means of the previously described model (*loc. cit.*), but in order to illustrate the second case it was necessary to devise a tervalent nitrogen model, the valencies of which could readily be inverted. The new model was constructed for this purpose (a model was first constructed in April, 1912). The central rod is then made of glass, and the valency arms, A, B, and C, represent the nitrogen tetrahedron of Hantzsch and Werner. Two of the valencies of this model are connected by thin rubber tubing to two arms of a carbon model, and the transformation effected, as has been previously described in the case of maleic and fumaric acids (*loc. cit.*).

The appearance of the nitrogen model, when completed, suggested to the author that it might be applied to represent some of the properties of the asymmetric carbon atom; the ends A, B, and C of the three arms, together with the end of the rod D, form the vertices of a tetrahedron, and consequently may represent the four groups attached to a carbon atom. The ease with which this tetrahedron is inverted renders the model suitable for the illustration of racemisation and Walden inversion

Fig. 1.

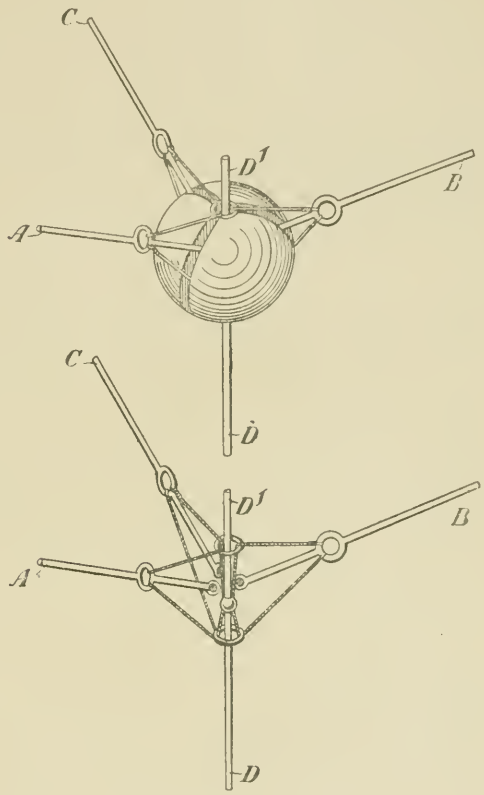
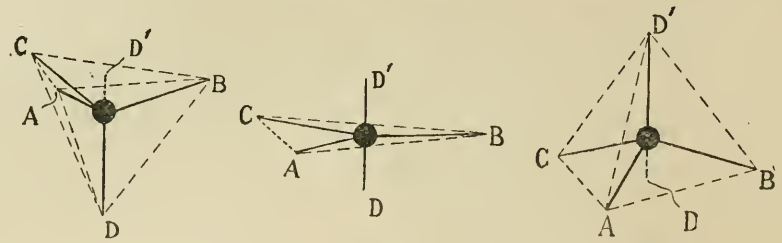


Fig. 2.

phenomena. Gadamer (*Chem. Zeit.*, 1910, xxxiv., 1004) had previously put forward the idea which it embodies, and had developed it fully to furnish an explanation of racemisation, and later has extended his theory to account for the differences in the behaviour of silver oxide and other bases on optically active chloro-acids (Frankland, *Trans.*, 1913, ciii., 722).

If the model represent a chemical molecule the group D may be replaced by another group with a change of configuration. In order to accomplish this, according to the Werner theory (*Ber.*, 1911, xliv., 881), the entering group must approach the molecule A, B, C, D from the side opposite to that occupied by the group D, and attach itself by means of its partial valencies at D′; if it is attracted to any of the other faces, no inversion would be obtained. Simultaneously with this addition, the group at D is gradually removed, and a corresponding movement of the other valencies occurs in a downward direction. The molecule will pass through an intermediate position II., in which the three valencies A, B, and C lie in one plane, and the fourth valency is divided into two halves at D and D′, and in this position the entering and extruded groups are attached to the carbon atom with equal force. In other intermediate positions the length of the central valency above and below the ball will indicate the relative strength of the attachment of the two groups. Finally, the groups



pass into the enantiomorphous position III., in which the group, originally attached at D, is completely removed.

Coloured balls or paper may be attached to the arms to represent the various groups.

(We are indebted to the Chemical Society for permission to use the woodcuts illustrating this Paper).

188. "*The Baly-Krulla Theory of Fluorescence. A Reply to A. W. Macbeth.*" By Edward Charles Cyril Baly.

In a recent paper (*Proc.*, 1912, xxviii., 271) A. W. Macbeth criticised the theory of fluorescence which Dr. Krulla and the author advanced (*Trans.*, 1912, ci., 1469). It seems that this criticism is based upon a misconception of the theory itself and of the processes which take place.

According to the theory the condensed force fields surrounding the molecules of a substance may be opened up in stages by the influence of a solvent and of light. These stages may be called 1, 2, 3, 4, &c., and each one absorbs light of different wave-lengths, λ_2, λ_3, λ_4, &c. Whereas previously only two of these stages had been recognised, the existence of several definite stages in the opening up of the condensed field of force has now been proved, and it is hoped very shortly to communicate the results of certain observations, which clearly show how by the use of suitable solvents several different stages can be produced absorbing different wave-lengths of light.

Now it is obvious that in the absorption of these light waves considerable damping must be present. If this were not so it is evident that the whole substance would on prolonged exposure become diactinic. This is, however, absurd; owing to the damping that is present the light actually does work against the chemical forces, and is therefore changed, probably into heat, so that as the result a continuous and constant absorption of the light takes place. It would seem that Macbeth has not taken this damping into consideration. He states that if the substance can exist in stages 1, 2, 3, &c., these forms must be in equilibrium with one another. This is not a correct assumption. If the stage 3 were present in equilibrium with 1 and 2, and if, according to hypothesis, $1 \rightleftarrows 3$ or $2 \rightleftarrows 3$ can be produced by absorption of light λ_3, it is absolutely certain that λ_3 would be absorbed out of a light source containing these waves. It is an experimental fact that λ_3 is not selectively absorbed as long as the solvent necessary is absent. In other words, if a fluorescent material which absorbs λ_2 and emits λ_3 is screened from λ_2 no trace of selective absorption of λ_3 can be detected. This rules out of court the assumption that stage 3 is normally present in simple equilibrium with 1 and 2.

Under the influence of the light a photodynamic equilibrium is set up, which is a very different thing from the chemical equilibrium assumed by Macbeth.

Macbeth's first criticism therefore seems absolutely to fail, first, because he assumes that stages 1, 2, 3 are in simple equilibrium; secondly, because he neglected the damping; and thirdly, because he assumes that the substance when screened from λ_2 must absorb λ_3.

Macbeth states further that the theory, although it cannot explain fluorescence, is more capable of explaining phosphorescence. It is now generally agreed that the two phenomena are really the same, and only differ in the relative velocity of the two processes, absorption and emission. In any case of fluorescence or phosphorescence there are two processes: the absorption of energy and the emission of energy. If the velocity of the second process is equal to or greater than that of the first, then the substance fluoresces, but if the velocity of the emission is slower than that of the first, then phosphorescence takes place, namely, the persistence of the emission for an appreciable time after the exciting cause has been removed. In certain cases the velocity of the emission of the energy is exceedingly small, and in these circumstances the energy absorbed in the first process remains stored up in the substance for a very long time unless the velocity of the emission is increased by some means, such as the application of heat, when the phenomenon is known as thermoluminescence. There seems, indeed, no reason to assume any difference between the two phenomena, and if a theory can explain one of them, it follows that it can explain the other.

According to the theory, the stages 1, 2, 3, . . . n, inasmuch as they are stages in the opening up of the condensed system of a single molecule, are intimately connected with one another, and although the process by which λ_2 is absorbed in the solvent is the only one which light itself is capable of bringing about, yet there can hardly be any objection to the probability that the disturbance to the whole system produced in this way will bring the next possible vibration periods into play, namely, stage 3 followed in less degree by stage 4, and so on.

It is known that, given the necessary external conditions, stages 3, 4, &c., are characterised by vibrations synchronous with wave-lengths λ_3, λ_4, &c.; if these vibrations are brought into play by means of some other vibration they will emit light of the same wave-length.

Macbeth seems to have fallen into an error as regards the relationship between the wave-length of the exciting light and the emitted light. In producing phosphorescence of wave-length λ_3, λ_3 is not absorbed.

There does not seem to be any difficulty in reconciling all observations as regards the relations between temperature and phosphorescence. In the first place, the conditions may occur when the process $2 \rightarrow 1$ is very slow indeed, with the result that the process $1 \rightarrow 2$ will take place with absorption of λ_2. After some time the whole system will have absorbed considerable energy. On heating the system, or in many cases simply by rubbing or shaking, conditions are produced that enable the process $2 \rightarrow 1$ to take place, with the result that a considerable amount of free energy escapes as heat, and the whole system gets disturbed, and some of the vibrations of stage 3 are called into play with emission of λ_3. In this process no λ_2 is emitted. Care must be taken not to look upon processes $1 \rightarrow 2$, $2 \rightarrow 3$, or $1 \rightarrow 3$ as being directly reversible, absorbing or emitting the same amount of light energy, for if this were so, it would simply resolve itself into a case of resonance phenomena. Macbeth has fallen into error here when he says that the reverse process $2 \rightarrow 1$ will be accompanied by the emission of light λ_2, as demanded by Kirchhoff's law. Kirchhoff's law has nothing whatever to do with the case, for it is not a case of black body radiation. The reverse process $2 \rightarrow 1$ is not accompanied by emission of λ_2, but probably by emission of heat, and the process is not reversible.

The next point is: Why do some substances fluoresce only at low temperatures when the free energy is less than before? The lowering of temperature will tend to produce a more completely closed system of force lines round the molecule. There must naturally exist a particular condition of this condensing together of the force lines for the particular type of fluorescence observed to take place, and it follows directly from the theory that this condition may be produced at low temperatures when it does not exist at higher temperatures.

It has been shown (*Trans.*, 1913, ciii., 91) that when a substance is opened up by a solvent and by light, the amount of light absorbed increases with the dilution up to a maximum, after which further dilution tends to decrease the amount absorbed, which is then followed by the disappearance of the selective absorption. There is thus an optimum condition of concentration as far as absorption of light is concerned. This agrees with and explains Lenard and Klatt's and Urbain's observations on phosphorescence, for these authors have clearly shown that there is always a definite condition of concentration of phosphorescence in the diluent at which an optimum of phosphorescence is observed. Clearly at this concentration the phosphorogen has its closed force field just sufficiently opened up, and in that condition best adapted to respond to the exciting vibrations in such a way that the next stages, 3, 4, 5, &c., are called into play. This optimum condition only refers to one particular temperature. At a much lower temperature that condition will not necessarily give the optimum, and indeed, perhaps, may not give any phosphorescence at all. Some other concentration will be more suited for the new temperature conditions, and whilst this new concentration may not suit the old temperature, yet on cooling, the phosphorescence or fluorescence makes its appearance.

A specific example may make this clearer, namely, the phosphorescence of strontium sulphide. Becquerel (*Ann. Chim. Phys.*, 1859, [3], lv., 5) found that this material gives at 200° an orange phosphorescence, and as the temperature falls the colour passes through yellow, green, and blue until at −20° it is dark violet. This observation has been confirmed for a great number of substances by Lenard and Klatt (*Ann. Physik.*, 1904, [4], xv., 225, 425, 633). The reason of this effect is that the phosphorescent spectrum consists of at least five separate maxima having the above colours, and as the temperature is changed the relative intensity of the various maxima alters, and in the case of the strontium sulphide the tendency, with decrease of temperature, is for the maximum of the phosphorescence to move towards the shorter wave-lengths. If the separate bands in the phosphorescent spectrum be called A, B, C, D, E, then at the higher temperatures A will be the most intense, and as the temperature falls, B, C, D, E, in turn, show the greatest intensity. Each of these corresponds with a definite stage in the opening-up process, and the optimum condition for each stage, provided that the quantity of diluent remains the same, depends on the temperature. By varying the conditions of diluent, similar variations in the relations between the intensities of the different phosphorescent maxima can also be obtained under constant temperature conditions.

This fact has an important bearing on the general theory. Since the whole phenomenon of phosphorescence is a property of diluted matter, and since the fall of temperature allows more and more free energy to escape from the system, it follows that the lower the temperature the less is the phosphorogen opened up by the diluent. The observations on phosphorescence therefore run *pari passu* with the observations on absorption, for here the more a compound is opened up by a solvent the nearer the absorption maximum lies to the red. In other words, the more complex the solvent-solute system, or, speaking generally, the more complex the system of the force field dealt with, the nearer to the red will be its absorption and also its phosphorescent or fluorescent maximum. Macbeth in his criticism, based on the fact that some substances do not phosphoresce or fluoresce at ordinary temperatures and do so at low temperatures, has really advanced observations which strengthen and confirm the theory.

Again, Macbeth attempts to draw an analogy between a spring in various stages of compression and the stages 1, 2, 3, &c. This analogy fails absolutely from the start, because it requires the same energy in different amounts to obtain the spring in the different stages of compression, while in the real case the stages 2 and 3, &c., require for their actual production not only a different solvent, but light of different wave-length. He also contradicts himself here, because in order for the analogy to be complete from his point of view, the states of the spring when in different stages of compression must be in equilibrium with one another, an assumption he made for the stages 1, 2, 3, &c.

Two further criticisms of Macbeth still remain to be dealt with. First, Nichols and Merritt's observations that the position of maximum fluorescence is independent of the wave-length of the exciting light, and that the latter may be on the red side of the fluorescent maximum. Macbeth says the processes are now reversed, and λ_3 is being absorbed and λ_2 emitted. This is by no means the case. An inspection of the absorption and fluorescent curves shows that these extend considerably on each side of the maximum in each case. They frequently, indeed, overlap, and therefore the very fact of Nichols and Merritt's discovery strongly supports the theory. The shape of the fluorescent curve is characteristic of the substance under the conditions of solvent and concentration. This fluorescence will be produced by any wave-length included in the absorption band, even if it happens by chance to be longer than those emitted. The substance responds to and absorbs the longer the wave-length, and it is natural to expect that it would produce the same effect as any other wave-length in the same absorption band. Nichols and Merritt also observed in the same paper (*Physical Review*, 1904, xix., 18) that if the fluorescent substance has a second absorption band of longer wave-length than the fluorescent light, the absorption of light in this second region does not produce fluorescence, which fact, of course, is in agreement with this theory.

Finally, Macbeth quotes the observation of R. W. Wood, who showed that while fluorescing with light of definite wave-length a substance exerts no increased absorption of that light. On a theory of optical resonance "fluorescence absorption" might be expected, and the fact that it has been proved absent argues strongly against any simple resonance as a basis of fluorescence and absorption. Nothing whatever in the theory makes it probable that fluorescence absorption should take place. A criticism based on the fact that it does not take place seems therefore somewhat irrelevant.

The general conception may be made clearer by considering it in the following way:—Light energy (λ_2) is absorbed and converted partly into heat and partly into light energy (λ_3). In ordinary circumstances this reaction is not reversible, because λ_3 is not absorbed, but it might be considered that under certain special labile conditions it does become reversible. The absorption of λ_3 during fluorescence would mean that the same reaction was taking place in opposite directions at the same time, and absorbing energy on both counts. Whether the process is reversible or non-reversible, there is no reason why λ_3 should be absorbed during fluorescence.

PHYSICAL SOCIETY.

Ordinary Meeting, June 13th, 1913.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper on "*Some Experiments on Tinfoil Contact with Dielectrics*" was read by Mr. G. E. Bairsto.

This paper describes some experiments showing how the accuracy of the different kinds of electrical measurements

that are made on condensers is influenced by the use of an imperfect tinfoil contact.

1. In connection with the measurement of the direct-current conductivity of a condenser having tinfoil armatures, the experiments of Mr. Appleyard (*Proc. Phys. Soc.*, 1905, xix., 724), in which the current a minute or two after the first switching on of the current was greater than that at the time of switching on, are referred to. These experiments go into the matter in more detail. By choosing a suitable dielectric—celluloid, which has a conduction current of a greater value than the rate of change of displacement current—it was found possible to greatly increase the magnitude of these secondary increases in current.

At very low pressures there is very little increase of current, and moreover what little increase there is over in a few minutes, but as the pressure is increased the secondary increase gradually becomes larger and takes longer to attain its maximum value. The maximum effect was reached at about 750 grms./sq. cm., when the increase of current amounted to 40 per cent, and the time required five and a-half hours. At very large pressures, when the contact becomes an intimate one, the increase of current becomes smaller again and the time required also smaller.

If the pressure is left on and the voltage removed for some hours a repeat test follows the same course, the current starting at the same value and attaining the same maximum value. Voltage has, therefore, quite as much effect as pressure in bringing about an intimate contact, and acts independently of it.

By considering the geometry of the tinfoil humps, an explanation of these various effects is given, and the different ways in which the pressure and the voltage increase the degree of contact between the dielectric and the tinfoil armatures are described.

2. While considerable errors are liable to be made in deducing the specific direct current conductivity of a dielectric between tinfoil armatures, the same is not true for measurements of the alternating-current conductivity. The influence of the bad contact is twofold. Firstly, it decreases the apparent capacity by inserting in series with the condenser under test a very large but still finite air condenser. This causes a decrease in the measured conductance. Secondly, because of the decrease in area of contact, it decreases the magnitude of that component of the conductivity which is independent of the frequency—*i.e.*, the purely ohmic conductivity.

By considering the system as equivalent to a leaky condenser in series with a very large capacity due to the air film, expressions are deduced for the equivalent capacity, conductance, and power factor, and these expressions furnish us with the means of separating out the two above effects.

It is shown experimentally, even under the worst possible circumstances, the dielectric being only lightly bound up with the interleaved tinfoil, that for telephonic frequencies the maximum difference between the observed conductivity and true conductivity is 15 per cent and of capacity is 5 per cent. With the condenser tightly bound with tape and wedges of wood inserted, the maximum difference was only 4·5 per cent in the conductivity and 2·5 per cent in the capacity.

3. Finally, the influence of imperfect contact upon the accumulation of residual charge is considered. It is shown that if we have a condenser with tinfoil armatures, as, for instance, tn the Franklin jar, with its rigid metallic coatings, the recovery of a residual charge is obscured by the presence of creeping surface charges coming out of the undischarged portions of the dielectric leading to an apparent residual charge much more than the true residual charge left in the dielectric.

Dr. J. A. FLEMING thought the paper contained much valuable information. He emphasised the difficulty and importance of getting rid of the air film. For many dielectrics, such as glass or indiarubber, pressure could not be applied. The tinfoil could he squeegeed on to the dielectric when the condenser was made, or the condenser could be put in a vacuum subsequently. For a constant condenser it was also necessary that there should be no chemical action between the metal plates and the dielectric such as occurred, for instance, in the case of copper foil and celluloid. He thought Mr. Bairsto's experiments on residual charges were very interesting. Theorists had attributed the whole effect to the properties of the dielectric, not to the bad contact between it and the electrodes. The paper was also useful in pointing out the pitfalls of experimental work on the subject.

Mr. R. APPLEYARD was glad Mr. Bairsto had adopted the direct reading method of examining the changes in dielectric resistance. The author had kept the current on till a steady deflection had been obtained. It was often more valuable to take the reading after a definite time, say, one minute. He did not think that the alternating current test in the second part of the paper had much bearing on the first part. The work on the residual charge was most interesting.

Mr. E. H. RAYNER remarked that it was assumed by all workers on the subject that the properties of the dielectric itself were not directly influenced by pressure, whereas this might in itself decrease the resistance of the dielectric. He would like the author to carry out pressure experiments on a silvered celluloid condenser.

Dr. A. RUSSELL agreed with the last speaker. Celluloid was far from homogeneous. The dielectric resistance was not a constant, but was a function of the applied voltage.

Mr. G. L. ADDENBROOKE emphasised the effect of heating of the dielectric due to the energy loss in it. He also remarked that the author had neglected surface conduction.

Mr. W. DUDDELL remarked that the paper showed the importance of a thin air film in the determination of the conductivity and capacity of a condenser. For standard condensers makers knew that if the air was not excluded the capacity would not remain constant. If a high voltage were applied to such a condenser and left on for some time the capacity afterwards would be found to be permanently altered. Even with as low a voltage as 200 volts we may get brush discharges into the air film.

Prof. C. H. LEES expressed his interest in the third section. He would like to know whether tinfoil electrodes under pressure would give the same residual discharge curve as mercury electrodes.

The AUTHOR, in reply to Prof. Lees, was sure it would give the same curve.

A paper "*On a Method of Measuring the Pressure of Radiation by means of Thin Metal Foil*" was read by Mr. GILBERT D. WEST.

The pressure of the radiation emitted by a carbon filamentl amp at a distance of a few centimetres is sufficient to cause a microscopically measurable deflection of the end of a suspended strip of gold or aluminium foil, and by this means the radiation pressure can be calculated knowing the weight of the strip. The results agree to within about 10 per cent with the energy content per cubic centimetre as measured by the initial rate of rise of temperature of a copper plate exposed to the radiation.

The best results are obtained by working in an atmosphere of hydrogen, 1 cm. to 2 cm. pressure, but good results are obtained with hydrogen at atmospheric pressure. Air at 1 cm. to 2 cm. pressure also gives good results.

The method involves no laborious adjustments, and the apparatus is not seriously affected by vibration.

Prof. C. H. LEES remarked that the point in the above paper was its extreme simplicity.

Dr. C. W. C. BARLOW (in some remarks communicated by Prof. Poynting) pointed out that the author ought to allow for the light reflected from the foil to the glass wall and back again to the foil. This would improve the agreement in the author's measurements.

A paper "*On the Emission of Electricity from Hot Bodies and the Quantum Theory*" was read by Dr. W. Wilson.

The paper gives a theory of the emission of electricity from hot bodies which is based on the quantum theory of energy. A formula connecting the thermionic current and the temperature of the emitting body is deduced. This formula closely resembles that of Richardson, and agrees slightly better with experimental results.

Prof. J. W. Nicholson thought the paper was a valuable one in that it connected up yet another phenomenon with Planck's quantum theory of radiation. It was probable that Planck's constant h was in some way an electron constant, and that the emission of energy was discontinuous because emission of electrons was discontinuous.

NOTICES OF BOOKS.

Metallic Alloys. By G. H. Gulliver, B.Sc., F.R.S.E., A.M.I.Mech.E., M.Inst.M. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

The text of this book is based upon various courses of lectures on alloys given by the author at the University of Edinburgh and at the Heriot Watt College, Edinburgh. It gives a systematic and thoroughly scientific view of the structure and constitution of binary and tertiary alloys, as well as a short account of the methods of investigation employed, and of the use of the microscope in general engineering practice. The second edition has been very greatly enlarged, and many new microphotographs and equilibrium diagrams have been added, so that the illustrations now number over 300, while the references to current literature are almost as numerous.

Organic Chemistry. By Howard D. Haskins, A.B., M.D. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

A complete survey of the facts of organic and physical chemistry which have an important bearing upon medical science is to be found in this book. The author has endeavoured to give a short description of every compound which should be known to the medical student, and the principles of physical chemistry are outlined. A course of practical work is described, including preparations, tests for purity, and methods of identification. A special feature of the text is the great number of structural formulæ given, with which the student is recommended to make himself thoroughly familiar.

Nitrogenous Soil Constituents and their Bearing on Soil Fertility. By Oswald Schreiner and J. J. Skinner. Washington: Government Printing Office. 1912.

This Bulletin contains a detailed account of the effect on seedlings of the different nitrogenous soil constituents. The investigation proves that some compounds are beneficial, while others, which appear to occur normally in soils, are harmful. Thus picoline carboxyllic acid retards growth, and guanidine produces effects similar to those due to disease. All the culture experiments were carried out under strict chemical control, so that all possibility of the interference of bacterial influences was excluded. The Bulletin contains a complete summary of the effects of organic compounds of all classes upon the growth of various plants, including the results of many tests carried out in previous researches.

Observaciones sobre el Método Crioscópico y Relaciones entre los Cuerpos Simples. ("Notes on the Cryoscopic Method and Relations between Simple Substances"). By Carlos E. Heredia. Buenos Aires: A. Guidi Buffarini.

In the first part of this thesis the results of many cryoscopic experiments are given, and some general inferences made from them; for example, the author has drawn attention to the fact that the maximum temperature of solidification is not necessarily equal to that of fusion. In the second part the question of the constitution of the elements is discussed and fundamental laws are formulated, showing how the chemical and physical nature of an element and also its type are functions of the atomic constitution which is a variable depending upon the degree of condensation of the atoms. The author expounds at length and with great intrepidity his views on force, energy, and matter, but does not appear to have made any material contribution towards the solution of the problem of their natures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 14, April 7, 1913.

Dehydration and Decomposition of Hydrates of Uranyl Nitrate.—M. de Forcrand.—When uranyl nitrate hexahydrate is dehydrated in the cold at atmospheric pressure two phases may be distinguished. During the first four or five days there is a tendency to form the trihydrate, and then when it is formed the loss of water becomes much slower, and stops completely when the dihydrate is reached. When the dihydrate is dehydrated at 98° in a current of CO_2 a monohydrate is formed, containing less than 1 per cent of uranic acid. A practically anhydrous salt can be obtained by dehydrating the dihydrate at 165° in a current of CO_2 containing nitrous vapours.

New Double Sulphate of Cerium and Silver.—Emm. Pozzi-Escot.—When a warm sulphuric acid solution of cerium sulphate is treated with a warm solution of silver nitrate an orange-yellow crystalline precipitate of a double salt is obtained. When it is washed and dried and the excess of sulphuric acid is removed by heating it to 400°, it is found that its composition corresponds to the formula $10Ce(SO_4)_2.6Ag_2.SO_4$. The anhydrous double salt is slightly soluble in cold water; when boiled with water it readily dissolves, undergoing decomposition.

Solubility of Thorium Oxalate.—A. Colani.—When thorium oxalate is dissolved in water containing at least 20 per cent of hydrochloric acid, chloro-oxalate is formed and oxalic acid is precipitated. The solubility of the oxalate in oxalic acid is less than in hydrochloric acid, and the solubility in the latter is greatly decreased by the presence of oxalic acid.

Action of Monosodium Acetylene on Alcoholic Iodides. Preparation of True Acetylenic Hydrocarbons.—Paul Lebeau and Marius Picon.—Chloride and iodide of methyl react at −50° on a solution of monosodium acetylene in liquid ammonia and allylene is obtained, $C_2HNa + CH_3I = NaI + CH_3.C{\equiv}CH$. The yield is about 96 per cent. Normal hexine can be prepared similarly from normal butyl iodide.

Catalytic Etherification in Dilute Solution. Preparation of Ethyl Acetate.—F. Bodroux.—The distillation of a mixture of acetic acid and propyl alcohol in presence of a concentrated aqueous solution of aluminium iodide leads to the formation of a large quantity of propyl acetate, and the production of this ether salt can only be attributed to the catalytic action of the dissolved salt. Ethyl acetate can be obtained from a mixture of ethyl alcohol and acetic acid if an aqueous solution of sulphuric acid is used as catalyst, and the proportion of organic acid etherified is greater the greater the concentration of the sulphuric acid in the aqueous solution.

No. 15, April 14, 1913.

Reduction of Magnesia by Aluminium.—Camille Matignon.—To reduce magnesia an intimate mixture is made with aluminium powder, which has been freed from fat by repeated washings with benzine and ether, in the

proportion of MgO to $\frac{1}{3}Al_2$. The mixture is pressed into tablets, and heated in an exhausted steel tube in a porcelain tube. At 1200° the magnesia is reduced and the magnesium is deposited in large crystals on the cooler part of the tube. The reduction is practically complete and constitutes a useful method of preparing magnesium.

Formation of Humic Matter by the Action of Polypeptides upon Sugars.—L. C. Maillard.—The author has already shown that humic matter can be prepared by the action of amino acids upon reducing sugars. The reaction is due to the groups NH_2 and COOH, and is shared by the polypeptides, which contain the same groups. Thus the behaviour of glycyl glycine exactly resembles that of glycocoll.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 8, 1913.

Solution of Constituents of Alluvial Sand by Subterranean Water.—F. Dienert.—When rain-water penetrates into sand in presence of carbon dioxide it dissolves calcium carbonate, magnesia, silica, and alkaline salts in definite proportions. But it has been shown that if the water circulates in sands in presence of an insufficient quantity of carbon dioxide it loses chiefly calcium carbonate, very little magnesia, no iron, aluminium, silicon, or alkaline salts.

Colour Reaction for Detection of Hyposulphites.—Emm. Pozzi-Escot.—To test for hyposulphite in a solution an equal volume of 10 per cent ammonium molybdate is added, and 5 cc. of pure concentrated sulphuric acid are run in by means of a pipette. In presence of hyposulphite a blue coloration is produced at the zone of separation of the aqueous mixture and the acid. If the concentration of the hyposulphite solution is greater than 1/5000, the blue zone is preceded by a more or less yellowish green zone. It is possible by means of this reaction to detect the presence of 0·00005 grm. of sodium hyposulphite.

Determination of Iodine in Iodotannic Syrup.—Emm. Pozzi-Escot.—A simple and rapid method of determining iodine in iodotannic syrup is as follows:—Twenty-five cc. of the syrup are diluted with 50 cc. of water. Ten cc. of chloroform or carbon disulphide are added, then 2 cc. of concentrated sulphuric acid and an excess of a saturated solution of potassium permanganate. The iodine is thus liberated, and dissolves in the organic solvent, and may be determined by means of a titrated solution of sodium hyposulphite.

Solubility of Certain Metallic Salts of Volatile Fatty Acids in Organic Solvents.—Henri Agulhon.—If the copper salt of an organic acid is produced in an aqueous medium by double decomposition, and the liquid is then shaken with certain organic solvents, the latter in certain cases extract all or part of the copper salt formed. The amount extracted is a function of the molecular weight of the acid used. Thus, whatever the solvent none of the salt is extracted in the case of formic or acetic acids. With propionate a light blue coloration appears in acetic ether, the aqueous solution remaining deeply coloured. In the case of butyrate an intense blue coloration is produced with acetic ether, ether, chloroform, amyl alcohol, while the aqueous solution becomes colourless.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 6.

Vapour Pressure of Liquid Tin Amalgams containing Small Amounts of Mercury.—A. Sieverts and H. Oehme.—The vapour pressures of liquid tin amalgams containing from 0·8 to 8 per cent of mercury are nearly proportional to the concentration of the dissolved mercury between 300° and 360°, and for pressures from 2—70 mm. Hg. Two single series of experiments with 2 and 10 per cent Hg gave the same result for 515° and 528°, and a pressure interval of 173—886 mm. Hg. Thus the solution of monatomic mercury vapour in liquid tin follows Henry's Law, while in the solution of diatomic gases in metals the quantity dissolved is proportional to the square root of the gas pressure.

Aromatic Telluretin Compounds.—Karl Lederer.—The methyl ether of bromacetic acid unites with diphenyl telluride to give a stable compound of formula $(C_6H_5)_2TeBr.CH_2.COOCH_3$, corresponding to the sulphur compound $(CH_3)_2SBrCH_2.COOH$. The bromine atom can be replaced by chlorine, and a picrate of similar composition can be obtained. The ethyl ether of bromacetic acid also combines with diphenyl telluride, but the compound formed is less stable than the methyl compound. When silver oxide acts on the ester of diphenyl telluretin bromide the bromine atom is replaced by hydroxyl and the ester is saponified.

Tetraphosphorus Trisulphide and a new Phosphorus Oxy-sulphide, $P_4S_3O_4$.—Alfred Stock and Kurt Friederici.—Tetraphosphorus trisulphide is very stable in absence of air and moisture when the temperature is raised, and solid P_4S_3 is very stable towards air. When oxygen is led through a solution of P_4S_3 in carbon disulphide in absence of moisure a new oxidation product, $P_4S_3O_4$, is obtained. It is a yellowish white heavy powder which decomposes when heated. It is very readily attacked by water, and gives a yellow solution with caustic soda. When ozone acts on P_4S_3 solutions, higher oxidation products are obtained. These resemble $P_4S_3O_4$ in their behaviour, but give a colourless solution with caustic soda.

MISCELLANEOUS.

Royal Society of Arts.—The Annual Meeting of the Royal Society of Arts was held on Wednesday, June 25th, Lord Sanderson, G.C.B. (Chairman of the Council), in the Chair. The usual Report recording the Proceedings of the Society during the past year was read. H.R.H. the Duke of Connaught was re-elected President, with the usual number of Vice-Presidents and Council. Thirty-five new Members were elected, making a total of 238 elected during the Session, the 159th of the Society.

Royal Society of Arts.—Award of Medals.—The Council of the Royal Society of Arts have awarded the Society's Silver Medal to the following readers of papers during the Session 1912—13:—

Dr. F. Mollwo Perkin—"Natural and Synthetic Rubber."
Joseph Pennell—"The Pictorial Possibilities of Work."
Henry J. Wilson—"The Education and Employment of the Blind."
E. Russell Burdon, M.A.—"The Development of Research Work in Forest Products."
Frank Bailey, M.Inst.C.E.—"Electric Supply in London."
Walter C. Hancock, B.A., F.I.C.—"The Physical Properties of Clay."
H. V. Lanchester, F.R.I.B.A.—"The Design and Architectural Treatment of the Shop."
F. G. Ogilvie, C.B., LL.D.—"The Science Museum."
Axel Welin, A.I.N.A.—"Life-saving at Sea."
Sir Bradford Leslie, K.C.I.E., M.Inst.C.E.—"Delhi, the Metropolis of India."
J. Forrest Brunton—"The City of Karachi."
N. G. Cholmeley, C.S.I., late Commissioner, Magwe Division, Burma—"The Oil-Fields of Burma."
Sir John Benton, K.C.I.E.—"Irrigation Works in India."
W. H. Warren, LL.D., M.Inst.C.E., M.Am.Soc.C.E., Dean of Faculty of Science and Challis Professor of Engineering, University of Sydney—"The Hardwood Timbers of New South Wales."
C. E. W. Bean, M.A., B.C.L.—"The Wool Industry in the British Dominions."
The Right Hon. Sir Joseph George Ward, Bart., K.C.M.G., LL.D.—"New Zealand: an Ideal Place of Residence."

THE CHEMICAL NEWS.

Vol. CVIII., No. 2798.

ACTION OF SEA-WATER ON FLANGES USED IN MARINE ENGINEERING.

By SERGIUS KERN, M.E., St. Petersburg.

Bronze flanges used in marine engineering were placed in sea-water (Atlantic Ocean composition) for a period of two months. Before suspending them in a wooden box, by ropes, they were turned and polished.

Composition of Flanges.

	Cu (per cent).	Sn (per cent).	Zn (per cent).
1.	90·0	3·5	6·5
2.	89·5	4·5	6·0
3.	87·0	8·0	5·0
4.	88·0	10·0	2·0

Weight of Flanges before Immersion.

	Pounds.
1.	27·73
2.	27·82
3.	27·48
4.	27·55

After two months the flanges were taken out of the bath of sea-water. On the surface they were bright; only here and there a small film of Cu_2O was observed.

Weight of Flanges after Immersion.

	Pounds.
1.	27·70
2.	27·79
3.	27·45
4.	27·51

The mechanical tests of test-pieces, cast with the flanges, were as follow:—

	Breaking strain. Tons per sq. in.	Elongation in 2 in. Per cent.
1.	15·15	34
2.	15·68	28
3.	15 77	31
4.	15·04	18

These experiments were made in order to show that the flange alloy No. 2, which was found by us to be the best for brazing purposes, corrodes not more than flange-alloys Nos. 3 and 4, prescribed by the Russian marine authorities.

Precipitation of Aluminium Hydroxide by Bromine from Aluminate Solutions.—W. Jakób. Bromine precipitates pure aluminium hydroxide from a boiling alkaline aluminate solution, and the reaction is quantitative and can be used to separate aluminium from chromium. The solution containing the two metals must first be treated with sodium hydroxide solution, drop by drop, till the precipitate dissolves. Then bromine water is added to the cold solution till the green colour is replaced by yellow. The solution is boiled and the aluminium hydroxide separates in a compact form. To remove the last traces of chromium from the precipitate the liquid is decanted off, and the precipitate is treated with water containing ammonia and ammonium nitrate, boiled for a few minutes, and filtered off. The small quantities of precipitate clinging to the walls of the flask are separated by means of dilute nitric acid, and added to the main bulk after neutralisation with ammonia. The method is not suitable for the precipitation of aluminium hydroxide in presence of sulphuric or boric acids.—*Anzeiger der Akademie der Wissenschaften in Krakau*, 1913, I. A.

ESTIMATING THE QUALITY OF PAPER.*

The Microscopical, Physical, and Chemical Tests of the United States Bureau of Standards.

It is a well recognised fact that an accurate knowledge as to the materials and chemicals entering into the composition of a paper is of great value to every paper maker who may be called upon to match a given sample. Manufacturers at present must depend on their personal judgment for such information, and the ability to correctly judge papers may only be acquired by long years of experience. To such an experienced man the first look at a particular sheet of paper reveals the general class to which it belongs, whether writing, printing, wrapping, board, &c. A second glance reveals the relative grade into which the particular class is subdivided. This preliminary information at once brings to the mind of the experienced man a picture of the general process of manufacture required to produce such a paper. By the use of his sense of smell he, in many cases, is able to determine whether it is animal sized or not; he presses his tongue against the sheet and says whether it is "water-leaf" or "sized" paper, and whether "slack," "medium," or "hard" sized; if a coated paper his tongue will indicate it. Upon closer inspection and a liberal use of the sense of "sight" and "touch," he is able to estimate the weight per ream, the thickness of the sheet, the fibre composition, and general method of treatment in the beater room, on the machine, and in the finishing room. He may also be able to give an estimate of bursting strength and general folding quality. The result of this method of testing is only comparative, and therefore lacks fundamental necessity of numerical expression for record purposes.

At the present time there is developing, both within and without the paper trade, a growing interest in the subject of paper testing. There is a demand on the part of the buyer for better methods to enable him to determine the quality of a paper. That there is this growing interest in the subject and a general demand for standard methods of testing is most conclusively shown by the work which is being accomplished in the commercial paper testing laboratories that are starting up in various parts of the country.

This increasing general interest in paper testing has been the cause of developing a series of tests that apply both to the physical and chemical properties of a paper. These tests are not meant to give absolute values, but if due care is exercised in the selection of a representative sample and in making the necessary tests, then numerical values will be obtained which to a large degree indicate something of the quality of a paper. Such a method offers the only means whereby a record of a paper may be kept.

In this discussion of paper testing, it should be distinctly understood that these tests do not cover every quality of property a paper may have. The degree with which one sample is a colour match for a second sample must depend upon the ability of the eye of the individual. The matter of "finish" is a second property, which so far cannot be expressed numerically, and for which there are no physical tests. The degree with which one sample conforms to another in finish is purely a personal element, and depends upon the experience of the individual.

At the present time there are no physical methods by which an accurate comparison may be made to determine when a paper contains a larger amount of dirt than is acceptable, or just what degree of "wild formation" shall render a paper non-acceptable. These two properties of "dirt" and "formation" are left to the judgment of the individual, and depend on a hazy mental idea of what he individually believes to be a point beyond which a paper

* Paper read at a meeting held under the auspices of the Bureau of Standards at Washington, D.C., Jan. 13, 1913. From the *Chemical Engineer*, xvii., No. 3.

becomes undesirable for the particular purposes for which it was intended.

The laboratory testing of a sheet of paper then narrows itself down to determining those properties which have a nearly fixed value or may be expressed in definite numerical terms. These values are such that when due care is exercised two or more individuals using the same methods and samples and working independently will obtain duplicate results. In other words, such methods very largely eliminate the personal element of the individual wherever the properties of a paper may be given a numerical value.

The general examination of paper may be subdivided into three parts as follows :—

Microscopical examination.

Physical tests.

Chemical analysis.

A microscopical examination will disclose the kind or kinds of fibres from which a given paper was made, and the experienced man will with considerable accuracy be enabled to estimate the proportions of various kinds of fibres used. The microscope also helps to indicate how much a stock has been beaten.

The testing to determine the physical properties of a paper is divided into determining: weight per ream, thickness, bursting strength, tensile strength, folding endurance, expansion, and absorption.

The chemical analysis will disclose the amount of ash retained and the amount and kind of size used. A chemical examination will also give much information in regard to colours used. All of this information is of the utmost importance in determining the quality of a paper.

The principal purpose of a microscopical examination is to determine what fibre or fibres were used in making a paper, and then to estimate the relative proportion of each on a basis of 100 per cent for the total fibre composition. Such an examination requires the following apparatus: beakers, test-tubes, slides for microscope, two long pointed steel dissecting needles, Bunsen burner, and tripod stand (or other means of heating sample), one large bottle of a ½ per cent solution of caustic soda, one small bottle of 25 per cent hydrochloric acid, six small dark coloured glass bottles, with dropping stoppers for stains, small pieces of filter paper, and a microscope which for ordinary work should be capable of magnifying about forty-five times. The binocular microscope will be found to be best suited for estimating work where it is desired to study the markings and special characteristics of a fibre, then a microscope capable of magnifying from 150 to 200 times should be used.

As all vegetable fibres are highly transparent and almost entirely colourless, when seen under the microscope, it is very necessary to use some staining solution to colour the fibre in order to bring out their size and shape and general markings. The best stain for this purpose is the so-called "Herzberg" stain, which is what is known as a selective stain, that is, it has the property of giving a yellow colour to most uncooked fibre, such as mechanical wood; chemical woodpulps are coloured in indigo blue; and cotton, linen, and some other fibres are coloured in wine red.

The staining solution is made up as follows :—

Solution A.

Zinc chloride	20 grms.
Water (preferably distilled) ..	10 cc.

Solution B.

Potassium iodide	2·1 grms.
Iodine crystals	0·1 grm.
Water (preferably distilled)	5·0 cc.

Dissolve A by adding the water to the zinc chloride in a glass beaker.

Dissolve B by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 cc. of water.

The two solutions — A and B — are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off and divided between two of the dark glass bottles with the dropping stoppers. All iodine solutions will fade in light, and should, therefore, be kept in the dark as much as possible.

It is a very good plan to use two more of the dropper stoppered bottles to keep a concentrated solution of zinc chloride and water in one and a concentrated solution of potassium iodide and iodine in water in the second; these two solutions will be found handy in adjusting the Herzberg stain.

The preparation of a sample of paper for the microscope is as follows :—Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a beaker and covered with ½ per cent caustic soda solution, the whole mass is then brought to boil over a suitable heating device. After boiling for about a minute, the liquid is poured off and some tap water added to wash out the caustic soda, and two or three drops of a 25 per cent hydrochloric acid solution added to neutralise the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper is pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test-tube and the test tube about half filled with water. Care must be exercised to rinse the hands after working each sample, to keep from contaminating the sample following. The test-tube is then shaken vigorously until the paper has been entirely broken up and the fibres are well separated. A few fibres are next removed on the point of the microscope needle from the test-tube, and a small sample is placed on each end of one of the microscope slides. The slide should be held in the holder over some black surface, as it is a great help to the eye to look at the white fibres against a black background. The wet fibres on a slide may best be dried by covering them with good filter paper and left for a few minutes to dry in the air.

The fibres are thoroughly dried and a drop of the Herzberg stain is added, and then the fibres are well "teased" out by the use of two microscope needles, a cover-glass is placed upon the fibres and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper, and the slide polished with paper or cloth.

The slide is next placed under the microscope, and after studying the various fields an estimate of the proportion of each of the various kinds of fibres may be given.

It is best to use four stains for this work, that is, each stain is of slightly different strength, as each one gives the best results on certain fibres. For example, a stain that clearly brings out the wine-red colour on cotton and linen fabrics, as a rule, usually does not give the best blue colour on bleached soda and sulphite pulp; the same stain on ground woodpulp has almost no effect at all.

In making up a stain to produce the best colour on the particular fibre, the following points should be remembered :—

Two or three drops of water added to a good stain for rag and bleached chemical wood will tend to fade out the wine-red colour, the blue colour will remain nearly unchanged, and the yellow colour on ground wood will be brought out very much clearer. In other words, a good rag stain, when used on ground wood, produces almost no colouring of the ground wood fibres.

The addition of two or three drops from the bottle containing the concentrated solution of iodine and potassium iodide, in water, will produce a deeper wine-red on rag fibres, while the addition of a few drops of concentrated solution of zinc chloride in water will produce a deeper blue on chemical wood fibres.

It should be remembered that these iodine solutions

will continually fade out, and that the best results may only be obtained when the stains give the proper colours.

The easiest and best way in which to secure a stain of the right colouring capacity is to keep on hand the following pulps: Bleached soda and sulphite pulps, unbleached sulphite, ground wood, and beaten rag stock. The rag stock may most easily be secured by using a sheet of good quality of filter paper, which is always made from "all rag" stock. Now take small bits of the bleached soda and bleached sulphite pulp and thoroughly mix them, after first separating them in water in a test-tube. Place a small sample on a microscope slide, thoroughly dry the fibres, add one drop of stain, separate fibres with the needles, place cover glass in position, and place slide under microscope. Each fibre seen should be of a blue colour, the sulphite fibres appearing much wider and longer than soda fibres, and should show a lighter blue colour, as the fibre is more translucent than a soda fibre, while the soda fibre should take a darker blue colour.

Soda and sulphite fibres should show a slight colour difference, and soda fibres being coloured a darker indigo blue, while sulphite fibres should be coloured a lighter indigo blue. If this colour difference is not clearly brought out, then either water or zinc chloride solution should be added, depending on whether it is desired to weaken or deepen the colours.

Some rag fibres should now be added to the test-tube, and a second slide made up, using a bottle of stain which is intended to produce best results on mixture of rag and woodpulps. This second stain is adjusted by adding water, zinc chloride, or iodine-potassium-iodide, or all as may be needed, until the three fibres, soda, sulphite, and rag, are all clearly brought out.

A third stain should be prepared for such papers as may contain ground wood by using mixture of ground wood and unbleached sulphite, and then adjusting the stains to give the best colours. The proper yellow for ground wood is the lemon yellow, never an orange yellow, as then the sulphite pulp is too slightly coloured and ground wood estimates are necessarily too high.

The experienced man may by using this method get some very surprising results. The Bureau of Standards believes that in papers containing mixtures of rag and bleached chemical wood, a careful microscopical estimate is well within 5 per cent of the correct fibre contents. For papers containing ground wood, especially where the percentage of ground wood is high, then the degree of accuracy is within 10 per cent of the correct fibre contents.

For laboratory use, the quickest sheet weighing device is the quadrant paper scales, so graduated that the corresponding ream weight—either 500 or 480 sheets—is read off directly in pounds.

Thickness of a paper may best be determined by the use of a spring micrometer having a hand that travels around a circular dial. This dial is graduated into thousandths of an inch and may be read to ten thousandths. In using such a gauge care should be taken to see that the pressure on the paper is constant, and also that the pressure surfaces are large enough not to compress the paper.

The bursting strength of a paper is determined with a machine by which the paper is firmly clamped against a rubber diaphragm, through which the pressure is applied to a circular area of the paper measuring one square inch. The actual pressure of the liquid under the rubber diaphragm required to burst the paper is registered on a carefully calibrated pressure gauge, reading pounds per square inch. An average of ten readings is taken as the correct bursting strength.

The tensile strength of a paper is determined upon a suitable machine, capable of accurately recording the tension required to break a strip of paper, when held at each end by suitable clamps, and the clamps are moved apart until breaking of the paper occurs.

The folding endurance is measured on a machine in which a strip of paper of definite size is clamped. The clamps are held apart under definite tension and the paper is caused to bend back and forth upon itself until the fibres wear through at line of folding. The number of double folds is recorded automatically by a suitable device.

Expansion of a paper may be determined by submitting the paper to different atmospheric conditions and noting resultant size of sheet at each change in the atmosphere.

The measure of absorption of a paper is the height to which, in a given time, a liquid will rise by capillary action, when one end of a vertically held strip of paper is immersed in water. This test, as well as all physical tests, must be made under a uniform condition of humidity.

The work of the paper laboratory at the Bureau of Standards comprises the testing of papers for the government service and the general public; also a study of methods of paper manufacture for the purpose of obtaining information of value in the preparation of government paper specifications. Information thus obtained is also at the disposal of the general public who may be interested in selling or buying paper under definite requirements.

It is not the intention of this bureau to go into general commercial paper testing, for the reason that there are regular commercial laboratories that are well equipped to do this work. Tests in dispute between outside parties will be taken up as an absolutely disinterested referee; in such case the bureau will very willingly give all possible assistance.

The equipment of the paper laboratory is at the service of the paper manufacturer as well as the user of paper for the investigation of problems of wide general interest, and it is desired to impress upon the trade and the general public that they are always welcome to such information as we may possess, provided such information does not come to us in a confidential manner.

The United States Government throughout its various branches consumes 40,000,000 lbs. of paper each year. This large amount of paper includes almost every grade or kind on the American market. The acceptance or rejection of such a large and varied amount of paper necessarily involves good judgment on the part of the paper inspector, together with an intimate knowledge of the manufacture of all kinds of paper, and a knowledge of the various uses to which each grade may be put. Is it reasonable to expect to find one or even two men who combine such a knowledge?

It is the firm belief of the Bureau of Standards that all manufacturers and users of paper will readily recognise that a correct set of definite chemical and physical tests, when carried out under uniform conditions, will give more reliable results than could be obtained in any other way. It is also the belief of the Bureau of Standards that a knowledge as to the nature of our methods of paper testing, as well as the manner in which a paper specification is developed, will tend to convince the trade of the fairness with which this work is carried on.

Royal Institution. — A General Meeting of the Members of the Royal Institution was held on July 7th, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Prof. E. Rutherford was elected a Member. The Chairman announced the decease of Her Grace the Duchess of Northumberland, and the following resolution was passed unanimously:—Resolved, That the Managers and Members of the Royal Institution of Great Britain at the General Meeting this day, desire to record their sincere sympathy and condolence with his Grace the Duke of Northumberland, President of the Royal Institution, and with the House of Percy, on the decease of Her Grace the Duchess of Northumberland.

A GASEOUS SPRING CONTAINING A HIGH PERCENTAGE OF HELIUM.

By E. CZAKÓ and L. LAUTENSCHLÄGER.

SINCE 1895, when Ramsay (CHEMICAL NEWS, 1895, lxxi., 151) first succeeded in isolating helium, this gas has been found in a large number of minerals, wells, and in gases issuing from the earth's crust. Of those who subsequently took up the subject after Ramsay, Prof. Kayser, of Bonn (CHEMICAL NEWS, 1895, lxxii., 89; *Chem. Ztg.*, 1895, S. 1547), was one of the first to identify helium in natural gaseous springs. By an examination of the hot springs of Wildbad, a resort in the Würtemberg division of the Black Forest, he succeeded in obtaining from 430 cc. of a sample of the gases, which chiefly contained nitrogen, 9 cc. of rare gases containing helium and argon, which corresponds to 2·1 per cent rare gas content.

During some researches which we have lately carried out, and which we have already published along with a detailed description of the apparatus and experiments (Sieveking and Lautenschläger, *Phys. Zeit.*, 1912, xiii., 1043; E. Czakó, *Zeit. Anorg. Chem.*, 1913, Bd. 83), we were able to repeat the investigations on the gases obtained from the hot springs of Wildbad. Commencing with about 1800 cc. of the gases, we obtained, as the mean of several concordant analyses, the following figures (which are corrected for the presence of air):—2·79 per cent carbon dioxide, 94·94 per cent nitrogen, 1·56 per cent argon, and 0·71 helium, thus giving us a value of 2·27 per cent for the rare gas content, a result which agrees satisfactorily with that obtained by Kayser.

Since the researches of Kayser are undoubtedly of real historical importance in the development of the study of the rare gases, we greatly desire to have this short note published in the columns of the CHEMICAL NEWS.

Chemisches Institut, Technische Hochschule,
Karlsruhe (Baden), May, 1913.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

WIRELESS TELEGRAPHY IN FRANCE AND ABROAD.

A RECENT statistic drawn up by the International Bureau of Berne shows that France, the cradle of wireless telegraphy, is at present relegated to the ninth rank as to the number of radiotelegraphic stations opened to the public. It is Canada that possesses the largest number of wireless telegraphic stations open to the general public. Canada has 32 stations. England holds the second place with 25 posts, then comes Russia with 22, Germany 20, Italy 20, Brazil 16, India 11, Spain 2, France 8, Denmark and Norway each 8, Japan 7, &c. But it must be noticed that over and above her 8 public posts, France possesses 11 radiotelegraphic stations for the War Department, the Navy, and the schools. But if France is in a state of evident inferiority as to the number of wireless telegraph stations, her situation is still more precarious if we consider the number of wireless telegraphy posts on vessels and commercial liners. Whereas England has 590 ships supplied with Hertzian posts and Germany 253, France has only 90 vessels that are supplied with radiotelegraphy. The number of radiotelegrams exchanged between the ships and the French posts of wireless telegraphy has increased from 876 in 1908 to 7694 in 1910, to 22,304 in 1911, and 33,786 in 1912. The number of words radiotelegraphed in 1911 reached 238,615, and 371,895 in 1912. It is especially the post of Sainte Marie de la Mer, near Marseilles, that has received and transmitted the greatest number of wireless telegrams. This increase of traffic led the postal administration to consider the advisability of the installation of a new wireless telegraph post at Marseilles.

NEW METHOD FOR MEASURING ALTITUDES.

Explorers often experience great difficulties in determining the altitude of mountains. M. Alphonse Berget, Professor at the Oceanographic Institute, Paris, in a work presented before the Academy of Sciences, has just indicated a simple method which renders it easy to calculate heights by means of the barometer. The employment of a table of logarithms is not necessary; two operations only are sufficient to enable one to measure altitudes rapidly.

The formula employed is simple; the height that is being sought is equal to the relation of the difference of pressure existing between the two places of which one wishes to measure the altitude, and the mean pressure between the two stations, multiplied by the sum of the mean temperature with a constant of 269. This product is multiplied by the coefficient 30. This formula may be thus represented:—

$$Z = 30\frac{D}{12}\ (T = 269).$$

By the help of this formula the altitude calculated is equal at about 1/500 m. to the result that would be found by the formula of Laplace.

THE DISAPPEARANCE OF THE SPOTS OF THE SUN.

Quite a whole school of meteorologists wish to connect the atmospherical phenomena with the spots of the sun. It is the spots or the faculæ which, it appears, are the cause of tempests and storms and even of earthquakes. When considerable spots are to be seen on the sun we may infallibly expect most direful catastrophes. Whether they will take place in France, in Europe, in Asia, or America, is not generally stated with any great precision, but if there is an earthquake in Japan, terrible cyclones in the West Indies, and storms and tempests in Europe, according to meteorologists these phenomena are incontestably due to the presence of spots in the sun, with the presence of which they coincide. The same coincidences are remarked for the changes of temperature. If it is hot, it is because a spot is passing on the solar equator. If it is cold, it is because the spots are absent or far removed from the median zone of the sun. If it rains in Paris, why then it is because a large spot has been perceived. But if the weather is fine, the sun is pure and shines without spot or facule. It is thus that everything relating to the weather is explained by the solar spots, but (and the question is one that is at present being discussed) when there are no spots what weather is to be expected?

According to M. Bailland, Director of the Paris Observatory, there have just been seventy days without any solar spot. So, then, ought not atmospherical life to be suspended, so to say, since the primary cause of rain, wind, seismic phenomena, as well as storm phenomena, no longer exists? Logically, then, perpetual fine weather should reign here below; we should now have a general calm, since all atmospheric perturbation of any importance originates from the solar spots, and these spots are absent.

Unfortunately for these theses, or rather these hypotheses, the world has not stopped going round during these seventy days of solar serenity. In France, as all over Europe, and in the whole world, there have been rain, storms, cyclonic and calm periods, and even important seismic shocks, from which especially the inhabitants of Bulgaria have suffered.

Consequently, since these terrestrial phenomena have taken place just the same without solar spots as with them, it becomes logical to conclude that the solar phenomena known by the name of spots or facula have no action whatever of cause and effect upon atmospheric variations; there are only coincidences, the strongest earthquakes, and inversely we may observe tempests and seismic shocks, more or less formidable, although no spots may be visible. That is what has just taken place in this present year 1913, and is what will happen again in some future year of the present century or in the year 2000,

either sooner or later; they are simple coincidences, nothing more.

As to being able to determine from an examination of the sun whether the summer of 1913 will be warm or cold, it would be as easy or not to foretell from the same spots whether on such and such a day it would be fine or not. First of all, it would be necessary to know whether on that day there are to be spots or not; now this prevision is almost impossible. The observers of the sun certainly do good work from a scientific point of view; what can be more beautiful than the study of the Royal day-star of our astronomic system? But when it comes to applying these studies to the forecast of the weather, either at short or long distances of time, why the heliacal science must refrain from pronouncing a judgment. Let solar astronomers be contented with foretelling magnetic fluctuations from the sun's spots; that is already a very fine result, but they had better not venture to foretell the state of the weather. It is an art, as said Lavoisier, that has its principles and its rules, but both are only on the surface of the earth and not in the depths of the heavens, nor in the mysteries of the Infinite.

The Speed of Glaciers.

"The Speed of Glaciers in Winter and the Inanity of the Thermic Theory of their Progression," such is the title of a study that has just been published by M. Vallot, Director of the Mont Blanc Observatory. From the numerous observations made by M. Vallot at the "Sea of Ice" in the massure of Mont Blanc, it appears that no calorific variation either diurnal or annual can penetrate into the interior mass of the glaciers, and that it may be considered as a river that is flowing on in its bed under the simple influence of weight, with a speed that is not sensibly different in winter to what it is in summer.

The Luminosity of Animals.

Many animals possess the power of becoming luminous at will. Glow-worms are the most striking example of this curious phenomenon. Many fish that live in the deep seas possess this same power of becoming luminous.

Scientific men have vainly tried to explain the mechanism of this luminosity. Prof. Armand Gautier has just communicated to the Academy of Sciences a notice of MM. Ville and Denien, of Montpellier, who explain this production of light by the oxidation of a substance secreted by luminous animals, called lophine. This organic azoted substance, under the influence of oxygen, emits a visible luminosity. Potash, in the presence of catalytic elements, such as the ferruginous matters of the blood, likewise provokes the oxidation of the lophine, and consequently forms light. Oxygenated water has also the same property.

In the organisms it is the unstable oxygen of the tissues catalysed by the ferruginous elements of the blood that produces the oxidation of the lophine, and renders animals luminous.

Metallic Beryllium.—Fr. Fichter and Kas. Jablczynski.—Metallic beryllium can be prepared by the electrolysis of a fused mixture of 1 molecule of NaF and 2 molecules of BeF_2. By repeated centrifugation of the impure preparation in a mixture of ethylene bromide and alcohol the comparatively light metal can be separated from the oxide which is present as impurity. The melting-point of beryllium is $1280° \pm 20°$. The fused metal is very hard, scratches glass, and is only slightly marked by a file. It is steel grey in colour (not silver-white, as Debray has stated). The specific gravity is 1·842 and the atomic volume 4·94. The resistance of beryllium towards water is caused by a layer of oxide formed on the metal. Hot nitric acid, either concentrated or dilute, readily dissolves it. —*Berichte*, xlvi., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President announced that, in future, a list of the papers to be read at each Ordinary Scientific Meeting will be advertised in the *Morning Post* on the Wednesday previous to the day of meeting.

Messrs. A. J. Berry and R. Robison were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alan Milsom Bailey, Lanhill, Chippenham; George Bernard Butler, 10, Malvern Street, Elswick Road, Newcastle-on Tyne; Alexander Houghton Hay, Essex Wharf, Narrow Street, Limehouse, E.; Harold Frank Tayler, 105, Barrow Road, Streatham, S.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—William Love Biggart; Archibald Joseph Brooks; William Rhys-Davies; Jack Cecil Drummond, B.Sc.; Horace Freeman; Roy Gonçalves Glenday, B.A.; James Joseph Hutchinson; Victor Lefebure, B.Sc.; Duncan James Macnaughtan; Ghulam Ali Mahamadi; Marius Maxwell; Ralph Richard Oliver; Percy Bernard Phillips; William Gilbert Saunders; Montagu George Smith; Ebenezer Rees Thomas, M.Sc.; Percy Cyril Lesley Thorne, B.A.; Jeremiah Twomey, M.Sc.; John Stewart Walker; Edwin Longstaff Watson; Ernest John Wilson, M.A.; Thomas Howard Young.

Of the following papers, those marked * were read:—

*189. "*Absorption Spectra and Chemical Reactivity.* Part III. *Trinitrobenzene, Trinitroanisole, and Picric Acid.*" By Edward Charles Cyril Baly and Francis Owen Rice.

The absorption spectra of trinitrobenzene, trinitroanisole, and picric acid were described, and it was shown how the closed force fields surrounding the molecules of these substances are opened up by the use of various basic solvents. In a previous paper (*Trans.*, 1912, ci., 1469) a theory of fluorescence was put forward based on the existence of several stages in the opening up of these closed systems. Whereas previously only one stage had been recognised, three stages have been proved to be produced with the three trinitro-compounds. It was shown how the results explain the formation of the picrates of the hydrocarbons and the nitration of the aromatic compounds.

Discussion.

Referring to the views on the origin of residual affinity advanced by Prof. Baly, and to the remark that previous explanations were "not satisfactory and connected," Dr. Flürscheim said that he was unable to discern any substantial difference between Prof. Baly's views and those he had himself published years before. In support of this he read some passages from one of his papers (*Journ. pr. Chem.*, 1907, [ii.], lxxvi., 185), in which the idea of an equilibrium between the combined and free affinity of an atom was clearly developed. He had repeatedly referred to this publication in subsequent communications to the Society, and based on it some further chemical generalisations, some of which he had already been able to confirm by chemical experiment.

Prof. Baly had merely used different words to express the same meaning. Thus, the term "force lines" used by Baly had already been previously employed by Hugo Kauffmann as a synonym for the term "chemical energy" adhered to by him (Dr. Flürscheim), and it was difficult to imagine chemical energy acting otherwise than in force lines. Similarly, the term "principal and secondary valencies," introduced by Werner and used by Prof. Baly,

was, when applied to the problem of residual affinity, merely a synonym for the term "affinity" used by him (Dr. Flürscheim).

He would therefore be glad to know in what way the views published by Prof. Baly differed from, and represented an advance on, those which he had himself published previously.

*190. "*Derivatives of* o-*Xylene*. Part V. 5-*Bromo*-o-4-*Xylenol and* 6-*Bromo*-o-4-*Xylenol*." By Arthur William Crossley and Dorothy Jessie Bartlett.

5-Bromo-*o*-4-xylenol, prepared by replacing the amino-group in 5-amino-*o*-4-xylenol by bromine, crystallises in glistening needles, melting at 80°. The *benzoyl* derivative forms transparent plates, melting at 51°, and the o-*nitrobenzoyl* derivative crystallises from ethyl acetate in transparent, rectangular plates, melting at 151—152°.

6-*Bromo*-o-4-*xylenol* was prepared from 5-nitro-3-*o*-xylidine by replacing the amino-group by a bromine atom and the nitro-group by hydroxyl. It separates from light petroleum (b. p. 80—100°) in masses of silken needles, melting at 103°. The *benzoyl* derivative crystallises from methyl alcohol in transparent, six-sided plates, melting at 85°, and the o-*nitrobenzoyl* derivative forms glistening needles, melting at 132°.

*191. "*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures*." Part II. By John Norman Collie and Hubert Sutton Patterson.

Since the authors' former communication on this subject (*Trans.*, 1913, ciii., 419), many further experiments have been made. That electrodes are necessary for the production of neon and helium has been disproved; for if a powerful oscillating discharge be passed through a coil of wire wound round a glass bulb containing a little hydrogen, helium with some neon can be detected in the residual hydrogen. It is necessary to free the gas in the bulb as completely as possible from mercury vapour. The experiment was frequently repeated in the same bulb, and even after many weeks' working, helium and neon could still be obtained from the apparatus. The hydrogen and oxygen used in these experiments was repeatedly tested in quantities up to 100 cc., but not a trace of helium or neon was found. The experimental bulb before use was heated to 250° and washed out with oxygen; the oxygen residue did not show the presence of either helium or neon.

Also an apparatus was made where the tube through which the discharge took place was surrounded by a vacuous outer tube. The wires connected to the electrodes in the inner tube passed through the outer tube in glass tubes, so that there could be no discharge from any electrodes in the outer vessel; in this case, also, helium and some neon were found in the outer vessel. The above experiment was made in the following manner. After the tube had been externally heated and pumped until no more gas would come off, a strong current was passed. At once hydrogen began to be evolved from the electrodes; this was pumped off, and an electric spark passed through it to see whether any oxygen was present. A very small contraction occurred; 4·6 cc. remained. This was then gradually put back into the tube, whilst a powerful current was passed through the tube, which was at the same time externally heated with a gas flame. At the end of three hours' sparking, 2·2 cc. of gas remained. This was again put back into the tube and the sparking repeated; at the end of another three hours it had shrunk to about 1·0 cc., and by further treatment it went to 0·4 cc. This hydrogen contained a trace of neon. At this point a crack appeared in the inner tube. From the outer tube only 0·4 cc. had been pumped off; this contained both helium and neon. The inner tube was broken up at once, the two aluminium electrodes were put into a hard glass tube, and fused by a blowpipe in a vacuum; 0·2 cc. of hydrogen was collected. The glass ends of the inner tube were powdered and also heated by means of a blowpipe in a hard glass tube that had been entirely pumped out. Too small an amount of hydrogen to be measured was pumped off. From the above experiment, 4·6 − 1·0 = 3·6 cc. of hydrogen had apparently disappeared. In the capillary tube between the two ends of the inner tube some black substance had collected where the tube had been very highly heated by the electric discharge. This substance was carbon, for on heating it with a little oxygen it suddenly burnt away with a bright flash, and the oxygen gave a milkiness with baryta solution. Many experiments have also been made with a double tube so constructed that mercury can be run up so as to fill the outer vessel, and drive the gas there up into a small capillary tube with a platinum wire fused through the end of it. The gas can under these conditions be examined by means of an electric discharge from the platinum wire to the mercury. During the whole of an experiment gas is perpetually appearing in the outer tube. It consists largely of hydrogen, together with traces of helium and neon, and of a gas that gives a spectrum of carbon. If it is sparked it rapidly decreases in volume, usually to about one-half and sometimes even less, the carbon spectrum almost entirely disappears, and the hydrogen (and the traces of helium and neon) remain. This same phenomenon also invariably occurs when testing for helium and neon. After the residual hydrogen has been exploded with excess of oxygen, and the residual oxygen has been absorbed by charcoal cooled in liquid air, the gas that remains should be pure helium or neon or a mixture of the two. The spectrum, however, is always a carbon spectrum, and it is only after sparking for some time that the carbon spectrum goes and the pure spectrum of helium and neon takes its place. There is always at the same time a diminution usually of over 50 per cent in the volume of the gas. This gas also is produced in the bulb, round which a wire has been coiled, and through which an oscillating discharge has been passed. It also is produced in a tube containing a piece of platinum foil, placed in the focus of a concave cathode of aluminium, bombarded by cathode stream, so that it becomes red-hot. At first, hydrogen is given, then hydrogen mixed with helium and some neon, then less hydrogen and helium, and some of the gas already mentioned that gives a carbon spectrum. After this apparently no more helium is produced, but an increasingly relatively larger amount of the gas giving the carbon spectrum. If this gas is sparked in contact with mercury vapour, it almost instantaneously disappears, and it has been found impossible to reproduce it, by heating the tube, or varying the pressure in the tube.

As it can be separated from the hydrogen in which it is found by exploding with excess of oxygen and removing that excess by means of charcoal cooled with liquid air, it appears to be a highly uncondensable gas, and not readily oxidised. This result, taken in conjunction with the fact that it gives a carbon spectrum, is very difficult to explain. It is possible that this gas may be the same as that discovered by Sir J. J. Thomson and called by him X_3.

Various experiments have also been made with electrodes other than aluminium. In the case of copper, interesting results were obtained. The hydrogen seemed to disappear more rapidly than when aluminium electrodes were used. Possibly this is due to the fact that a more powerful current can be passed through the tube, and the electrodes therefore heated to a higher temperature. The splashed copper was in parts of a black colour. Even after as much as 5 cc. of hydrogen had been absorbed by a tube, no amount of heating made the gas come off again. The copper splash was dissolved in aqua regia and evaporated to dryness, some water and a little hydrochloric acid added, and the clear solution of the copper salt was then tested with barium chloride. A small, white precipitate was obtained. This has been repeated many times; the copper splash always gives this precipitate. Presumably it is barium sulphate; but it is somewhat difficult to prove the presence of sulphur in the minute amount produced. The actual amount from four different experiments weighed about one-tenth of a milligrm.

Some of it was heated with a little sodium carbonate and carbon, and gave a faint brown stain on silver; also, with hydrochloric acid, a very faint odour of hydrogen sulphide. As ordinary glass contains traces of sulphur, four more experiments were made with lead glass tubes that are quite free from sulphur. Again in every case a precipitate was obtained in acid solution by barium chloride. Three other tubes with respectively magnesium, platinum, and palladium electrodes all gave this precipitate. Every conceivable precaution was taken to test the metals, the reagents, and the electrodes for sulphur, and, except in the case of soda-glass tubes, sulphur was invariably absent.

The results at present arrived at from the experiments given in this note are the following:—

(1) Electrodes apparently are not necessary for the production of the helium and neon.

(2) Hydrogen in considerable quantities can be made to apparently entirely disappear in tubes through which a heavy discharge passes.

(3) A gas is produced in the tubes that gives a carbon spectrum. It entirely disappears when sparked in contact with mercury. It is not readily condensed by charcoal cooled in liquid air, nor easily oxidised by sparking with oxygen.

(4) When copper, platinum, palladium, or magnesium are splashed off in an ordinary vacuum tube containing hydrogen, something is produced that, after dissolving in aqua regia, gives a precipitate in acid solution with barium chloride.

Note.—Only one of the authors (J. N. C.) is responsible for the statement that the metallic splashes give, after solution in acids, a precipitate with barium chloride. Since the paper was read he has made further experiments that probably account for its production.

(1) Copper electrodes were used. The solution of the splash in acids was evaporated in *silica* vessels. *No precipitate was obtained.*

(2) The same tube was used again, and the solution of the splash was divided in half. One half (*a*) was evaporated in glass test-tubes, the other half (*b*) was evaporated in silica vessels: (*a*) *gave a precipitate*, (*b*) *gave no precipitate.*

A blank experiment was made with the acids and considerable evaporation in glass test-tubes, and a precipitate was obtained with barium chloride in acid solution.

The hydrochloric acid had been boiled with, and then distilled from, solid barium chloride, and the nitric acid had been treated in the same way with barium nitrate.

There also might be another explanation of the precipitate. The copper electrodes were sealed to the platinum by a little silver solder; some of the silver splashes off; this gives silver chloride, that on evaporation with strong hydrochloric acid dissolves, and is reprecipitated on dilution and addition of barium chloride.

*192. "*The Rotatory Dispersive Power of Organic Compounds.* Part III. *The Measurement of Magnetic Rotatory Dispersion.*" By Thomas Martin Lowry.

A description was given of apparatus and methods for the measurement of magnetic rotations over a wide range of the visible spectrum.

*193. "*The Rotary Dispersive Power of Organic Compounds.* Part IV. *Magnetic Rotation and Dispersion in some Simple Organic Liquids.*" By Thomas Martin Lowry.

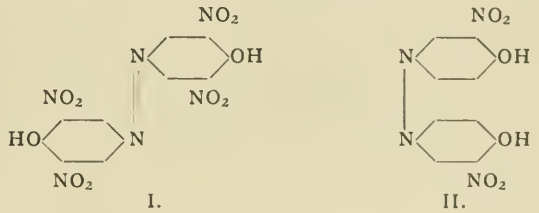
Numerical values were given for the magnetic rotation and dispersion in (1) inactive primary alcohols, (2) active secondary alcohols prepared by Dr. R. H. Pickard, (3) fatty acids, including active valeric acid, (4) ketones, (5) esters and paraffins prepared by Prof. Young, (6) carbon disulphide.

*194. *The Isomerism of* p-*Azophenol.*" By Philip Wilfred Robertson.

p-Azophenol, $HO{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_4{\cdot}OH$, as ordinarily prepared, forms yellow crystals containing one molecule of water; there appear, however, to be two yellow modifications, one of which yields, on heating, the anhydrous compound as a dark green, the other as a brick-red variety. Both of these forms have been shown to be stable in dry air under ordinary conditions; at higher temperatures the red is converted into the green, the transition temperature being about 50°. This is possibly not a case of polymorphism, because the difference seems to persist in solution.

In addition to this *a*-azophenol, Willstätter has obtained, by oxidation and subsequent reduction, a *β*-modification, a red substance incapable of being reconverted into the original compound by physical means. Hantzsch has shown that both substances have exactly the same absorption spectra, and calls this a case of homochromisomerism.

The chemical reactions of the two substances have now been examined. On bromination, they yield different tetrabromo-derivatives, melting at 252° and 271°, and these have also identical absorption spectra. On nitration, *a*-azophenol yields a tetranitro-compound (I.), whilst the *β*-modification, even with considerable excess of nitric acid, forms only a disubstituted derivative (II.):—



It is possible that this difference is due to stereoisomerism, as is indicated in the above formulæ.

Discussion.

Prof. Meldola considered that Dr. Robertson had made out a good case in favour of the stereoismerism of the two forms in the sense of their being the *syn*- and *anti*-modifications. He had no doubt the author had considered the possibility of quinonoid isomerism, since one-half of the molecule admitted of such rearrangement. He asked whether this point had been tested by checking the mobility of the hydroxylic hydrogens by preparing the methyl derivatives, and, if so, whether the two isomerides gave isomeric or identical methyl derivatives.

In reply to Prof. Meldola, Dr. Robertson said that the fact of the two isomerides having the same absorption spectrum precluded the possibility of either possessing a quinonoid constitution. The author differed from Prof. Baly in his contention that an equlibrium mixture in solution might yield two different substances on removal of the solvent, according to whether one started from one or the other isomeride.

*195. "*The Action of Ozone on Cellulose.* Part IV. *Cellulose Peroxide.*" By Charles Dorée.

Ozone acting on purified cotton-cellulose was stated to furnish a peroxide, recognised by its oxidising action on potassium iodide solution (*Trans.*, 1912, ci., 498). Doubts having been cast on the existence of this product, the question has been reinvestigated. In the absence of water, a small amount of peroxide alone is produced, but in air-dry material the quantity of peroxide formed is very much greater, and at the same time the solid insoluble acid and oxycellulose are formed (*loc. cit.*). The amount of "active oxygen" fixed by air dry cotton, mercerised cotton, and lustra-cellulose after eighteen hours' exposure to ozone was 0·0056, 0·0106, and 0·0248 per cent respectively. The peroxide is slowly decomposed on treatment with water, hydrogen peroxide being produced. It is decomposed to the extent of 25 per cent, after heating for two hours at 37°, and almost entirely after two hours at 95°. The activity soon disappears if the material is kept

in the air, but persists for some weeks in a dry atmosphere. The peroxide acts strongly on a photographic plate, sharp negative images of the fibres being obtained in twenty days at 14°, or in six hours at 37°. These properties recall the photographic action of the natural woods described by Russell (*Phil. Trans.*, 1904, cxcvii., 281, &c.), and were shown to be due probably to a similar cause, namely, the gradual production of hydrogen peroxide.

The question of the position in the cellulose complex at which the peroxide oxygen may be attached was discussed, together with the part played by the peroxide in the oxidation of cellulose by ozone.

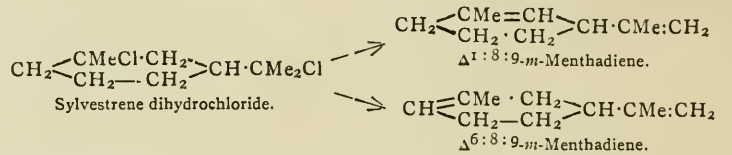
Discussion.

Mr. C. F. Cross believed that the author's paper would be found to explain these observations in terms of a cyclic formula for the unit (C_6) constituent group of the cellulose complex with the "potential" unsaturated position.

He called attention to current articles by H. Gebhardt (especially *Chem. Zeit.*, 1913, xxxvii., 663), discussing the constitution of cellulose from the point of view of its affinities for colouring matters. This author arrived inde pendently at similar conclusions.

*196. "*Sylvestrene. The Constitution of* d-*Sylvestrene and its Derivatives.*" By Walter Norman Haworth, William Henry Perkin, jun., and Otto Wallach.

The authors have been engaged on a detailed investigation of *d*-sylvestrene, prepared from the dihydrochloride by the elimination of hydrogen chloride, and they find that it is mainly a mixture of $\Delta^{1:8:9}$- and $\Delta^{6:8:9}$-*m*-menthadiene.



They have also prepared a large number of derivatives of sylvestrene and determined their constitutions.

197. "*The Refractivities of Acenaphthene and its Monohalogen Derivatives.*" By Holland Crompton and Wilhelmina Rebecca Smyth.

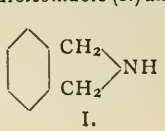
The following values have been obtained for the molecular refractions of acenaphthene and its monohalogen derivatives:—

	M_C.	M_D.	M_F.
Acenaphthene	50·84	51·33	52·84
3-Chloroacenaphthene ..	55·53	56·07	57·55
3 Bromoacenaphthene ..	58·97	59·58	61·22
3-Iodoacenaphthene ..	63·42	64·10	66·02

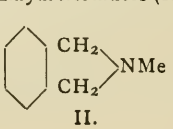
The molecular refraction, M_C, of acenaphthene, calculated from that of naphthalene, is 50·94, and in the case of the halogen derivatives, the values calculated for the molecular refractions from that of acenaphthene agree with the observed. There is therefore nothing abnormal in the behaviour of these compounds.

198. "*The Formation of Cyclic Bases from Aromatic Imides.*" (Preliminary Note.) By Edward Hope and Frederick Russell Lankshear.

The authors have studied the electrolytic reduction of phthalimidine and of N-methylphthalimidine (prepared from phthalimide and N-methylphthalimide respectively), and have succeeded in obtaining excellent yields of dihydro*iso*indole (I.) and N-methyldihydro*iso*indole (II.):—



I.



II.

The properties of dihydro*iso*indole thus prepared agree with those given by Gabriel and Pinkus (*Ber.*, 1893, xxvi., 2210) and by Fränkel (*Ber.*, 1900, xxxiii., 2809). As stated by the latter, methyl iodide reacts with dihydro*iso*indole, giving a mixture of the hydriodide and the methiodide.

N-*Methyldihydroisoindole* is a colourless oil with a strong basic odour, and boils at 195—196°/750 mm. It is very soluble in water, and readily distils over in steam, separating in the distillate as a sparingly soluble hydrate, which contains two molecules of water.

The compound also reacts vigorously with methyl iodide, giving a quantitative yield of the methiodide (m. p. 246°). This is identical with the methiodide obtained under similar conditions from dihydro*iso*indole.

This electrolytic reduction process renders simple the preparation of *iso*indole bases, which have hitherto been obtained only by somewhat laborious methods. The authors are engaged in an investigation of these bases, and are carrying out experiments with a view to apply the reduction process to a variety of similar imides.

199. "*The Action of Sulphur Dioxide on Copper at High Temperatures.*" By Clifford Morgan Stubbs.

The depression of the freezing point of copper by dissolved sulphur dioxide has been found to be about 2·54 times that expected if the molecules of the gas remained intact in the solution. This result can be explained on the hypothesis of a partial reaction of the dissolved gas with the molten metal according to the equation $6Cu + SO_2 \rightleftharpoons Cu_2S + 2Cu_2O$.

Complete reaction would give three times the depression calculated from the molecular formula SO_2.

It has been shown that this hypothesis of an equilibrium in the molten metal can be brought into harmony with the solubility results of Sieverts and Krumbhaar. The equilibrium pressures of sulphur dioxide in the univariant system Cu, Cu_2O, Cu_2S (all as solids) have also been measured between 700° and 1050°, the pressure rising in this range of temperature from less than one atmosphere to about seven atmospheres.

200. *The Change of Colour of Metallic Haloid Solutions.*" By Charles Scott Garrett.

Solutions of coloured metallic haloids in general undergo considerable changes of colour on varying the concentration, temperature, or solvent, as well as on the addition of colourless haloid salts. The phenomenon is connected with the presence of varying valency in the parent metal.

It was pointed out that these changes most probably are due to the formation of complex radicles of two types, acidic and metallic radicles, and by quantitative spectrophotometric measurements it has been shown how these two types of complex formation may be distinguished. Copper haloids form acidic complexes, whilst chromium haloids form metallic complexes, but the solvent must be regarded as playing some part in the change.

Bands of selective absorption due to the complexes were found in the case of cupric bromide, cupric chloride, and nickel bromide solutions, by photographing the saturated aqueous solutions in very thin layers.

In the typical cases of copper and chromium haloid solutions it was shown that the various parts of the absorption spectra may be attributed to various entities in the molecules of the salts.

201. "*Hydroxyazo-compounds. The Action of Semicarbazide Hydrochloride on the* p-*Quinones.*" By Isidor Morris Heilbron and James Alexander Russell Henderson.

As indicated in a recent communication (*Proc.*, 1912

xxviii., 256), the condensation products obtained by the action of semicarbazide hydrochloride on the *p*-quinones in equimolecular quantities must, from spectrographic evidence, be regarded as hydroxyazo derivatives. A further examination of these condensation products has, however, made evident that under certain conditions a few of these hydroxyazo-compounds undoubtedly react tautomerically as semi-carbazones. The authors find further that on salt-formation the hydroxyazo-compounds assume a quinonoid constitution, as is proved by the great similarity of their absorption curves with the typical quinone, tetraphenylquinodimethane. This compound shows a very characteristic band of great persistence in M/10,000 solution, differing in position from the band of *p*-benzoquinone and its homologues, but resembling closely the absorption curves of the nitrophenol salts, and the authors adduce from this that such salts are undoubtedly quinonoid.

A direct relationship has also been found to exist between the molecular weight and position of the absorption band in this series of similarly constituted compounds.

202. "*The Alkaloids of Ipecacuanha.*" (Preliminary Note). By Francis Howard Carr and Frank Lee Pyman.

In spite of the medicinal importance of ipecacuanha, very little is known about the alkaloids which it contains, although the subject has received a considerable amount of attention. A number of earlier investigations were carried out with a purified amorphous total alkaloid, formerly known as "emetine," but later Paul and Cownley (*Pharm. Journ.*, 1894, [iii.], xxiv., 111) showed that this product contains at least two alkaloids, emetine and cephæline, the latter being a phenolic base, and described methods for their separation and purification. They attributed to emetine the formula $C_{30}H_{44}O_4N_2$ or $C_{15}H_{22}O_4N_2$, and the cephæline, $C_{28}H_{40}O_4N_2$ or $C_{14}H_{20}O_4N_2$, whilst O. Hesse (*Pharm. Journ.*, 1898 [iv.], vii., 98), repeating the work at their request, preferred the formula $C_{30}H_{42}O_4N_2$ for emetine and $C_{28}H_{38}O_4N_2$ for cephæline. Hesse showed that emetine contains four methoxyl groups, whilst the results for cephæline lie between those required for two and three.

The subject has recently been reinvestigated by Keller (*Arch. Pharm.*, 1911, ccxlix., 512), who has brought out the important result that emetine forms a nitrosoamine, and therefore contains an imino-group. He regards it as a secondary tertiary base, containing two methoxyls and at least one hydroxyl group.

In the course of an extended investigation of these alkalcids, the authors have obtained results having an important bearing on the constitution of emetine and cephæline, and think it well to record briefly at the present stage some of their principal conclusions.

A large number of analyses of emetine, and of its hydrochloride, hydrobromide, hydriodide, and nitrate have now been carried out, and these indicate the formula $C_{29}H_{40}O_4N_2$ for this base. This formula is also in better agreement on the whole with the few results obtained by previous investigators than any of the formulæ suggested by them. Cephæline is probably correctly represented by the formula $C_{28}H_{38}O_4N_2$. These formulæ, which are supported by molecular-weight determinations, indicate that each alkaloid contains two nitrogen atoms.

In the stable neutral salts, the bases are combined with two equivalents of acid. Evidence of the existence of basic salts has also been adduced. In each base both nitrogen atoms are present as imino-groups; and these alkaloids are therefore disecondary bases.

Emetine contains four, and cephæline three, methoxyl groups, whilst the latter also contains a phenolic hydroxyl group. All the oxygen atoms contained in them are thus accounted for. Both alkaloids are optically active, the bases being lævorotatory, emetine having $[\alpha]_D - 22°$, and cephæline $\alpha]_D - 18°$, whilst the salts are dextrorotatory, anhydrous emetine hydrochloride $[\alpha]_D + 16°$ corresponding with $[\alpha]_D + 18°$ for the basic ion.

Emetine yields, on oxidation with ferric chloride in aqueous solution, a scarlet, crystalline hydrochloride, which is termed *rubremetine hydrochloride*. Being formed by the removal of eight hydrogen atoms from emetine, it has the formula $C_{29}H_{32}O_4N_2,HCl,6H_2O$. It melts at 127—128° (corr.), contains four methoxyl groups, and is monobasic. When emetine is oxidised with a large amount of potassium permanganate in aqueous acetone solution, 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid is formed, identical with the substance previously obtained by Goldschmidt by the oxidation of papaverine; *m* hemipinic acid has also been observed amongst the oxidation products.

Cephæline, on oxidation, behaves differently from emetine, ferric chloride giving rise to two crystalline oxidation products:—(i.) a *hydrochloride*, $C_{24}H_{24}O_7N_2,HCl,5H_2O$, melting at 249—250° (corr.), and containing three methoxyl groups but no hydroxyl group, (ii.) a *hydrochloride*, $C_{17}H_{21}O_6N,HCl,4H_2O$, melting and decomposing at 158° (corr.), after drying at 100°, and containing two methoxyl groups and a hydroxyl group.

A crystalline N-methyl derivative of cephæline, melting at 194° (corr.), has also been obtained.

The results are being elaborated and extended, and it is hoped to communicate them fully to the Society later in the year.

203. "*Dibenzoyldiaminoacetic Acid.*" By Paul Haas.

When α-hydroxyhippuric acid—

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CO_2H,$$

is heated to 150°, it is converted into dibenzoyldiaminoacetic acid, $(C_6H_5{\cdot}CO{\cdot}NH)_2CH{\cdot}CO_2H$, in a 40 per cent yield; the latter substance, on hydrolysis, decomposes into benzamide and glyoxylic acid.

204. "*The So-called Calcium β-Diglycerylphosphate.*" (A Correction.) By Frank Tutin.

In a paper published by the present author and Mr. Hann (*Trans.*, 1906, lxxxix., 1754), a calcium salt, melting at 249—250°, was described, which, on hydrolysis with dilute acids, gave a small yield of β-glycerylphosphoric acid. Analyses of the calcium salt mentioned gave results in harmony with the conclusion that it had the composition $C_{12}H_{28}O_{16}P_2Ca$, provided it were assumed that thirteen molecules of water of crystallisation were also present. It was therefore regarded as hydrated calcium β-diglycerylphosphate.

It has now been ascertained that this conclusion cannot be correct, since the calcium salt in question contains chlorine (about 38 per cent on the air-dried material). This fact, however, does not affect the identity of the β-glycerylphosphoric acid prepared by the hydrolysis of the calcium salt, the formation of which was one of the objects of the above-mentioned investigation.

205. "*Some Derivatives of Desylamine.*" By Alex. McKenzie and Fred Barrow.

The authors have studied the conversion of phenylaminoacetic acid into desylamine, with the primary object of aiding an investigation, which is at present in progress, on the isolation of the optically active modifications of the base.

α-Phthalyliminophenylacetyl chloride, when acted on by benzene and aluminium chloride, gave desylphthalimide (compare Pfaehler, *Ber.*, 1913, xlvi., 1700), from which desylamine can be obtained.

A mixture of desylphthalimide and dibenzoylstilbene was produced by the interaction of desyl chloride and potassium phthalimide in presence of nitrobenzene at 150—160°.

2 : 4 : 5-Triphenyloxazole was prepared by the dehydration of benzodesylamide and concentrated sulphuric acid.

The action of various Grignard reagents on desylamine hydrochloride has also been investigated.

(To be continued).

NOTICES OF BOOKS.

Iron and Steel. By O. F. HUDSON, M.Sc., A.R.C.S., with a Section on Corrosion by GUY D. BENGOUGH, M.A., D.Sc. London: Constable and Co., Ltd. 1913.

THE aim of this book—to put before students and practical men the elementary principles of the metallurgy of iron and steel—is well fulfilled, and it can be recommended as a good introductory text-book, describing the outlines of foundry practice, the properties of irons and steels, and the constitution of the iron-carbon alloys. The photo micrographs of the latter are well reproduced, and a clear explanation is given of the construction and interpretation of equilibrium diagrams. Dr. G. D. Bengough has contributed to the book a chapter on the corrosion of iron and steel, in which a full review is given of modern work and theories on the subject.

The Function and Scope of the Chemist in a Pharmaceutical Works. By CHARLES ALEXANDER HILL. London: The Institute of Chemistry of Great Britain and Ireland. 1913.

THIS lecture, which was delivered before the Institute in March, 1913, discusses some aspects of the work of a chemist in pharmaceutical works. The manufacture of pharmaceutical chemicals and preparations is treated in outline, and some account is given of the different processes involved. The control of raw materials, finished products, &c., is discussed shortly, and the effect of the analytical control of commercial products is made the subject of some practical remarks. The investigation or research work which may fall to the lot of a works chemist is considered, and the part he can play on the commercial or less technical side is also pointed out. The lecturer aimed at stimulating the activity of the works' chemist, and showing by actual examples how the man who has had a laboratory training but no experience in a factory may apply his knowledge to the best advantage of himself and his employer.

The Qualitative Analysis of Medicinal Preparations. By H. C. FULLER, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

THE task of determining the constituents of a mixed medicine is one which is exceedingly tedious and complicated, and ordinary text-books of analysis are of very little use, since they take no account of the possible mutual action upon one or another of the different drugs which may be present, while the numerous articles on the subject which have appeared in periodical literature are widely scattered and difficult of access. The author of this book has worked out a systematic scheme by which a medicinal preparation can usually be completely analysed, the ingredients being first separated into large groups, then into smaller groups, and finally identified as individuals. Some of the tests are new, while others have been brought together from various sources, and the scheme is really comprehensive, including all the usual medicinal substances.

Dairy Technology. By C. LARSEN, M.S.A., and WM. WHITE, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THIS book treats of the technology of the dairy, the preparation of dried and condensed milk, renovated butter, and various other dairy products. Analytical methods and the more purely scientific side of the subject are not treated in it, and throughout American methods and practice are chiefly discussed. But inspectors, dairy owners, and the marketers of dairy produce in this country can learn something from it. Copious statistics of city milk supplies are given, and plans for the improvement of the conditions under which milk, &c., is sold are suggested. The pasteurisation of milk is discussed, and the advantages and disadvantages of the process are compared at length, while methods of standardisation of milk and cream are also described, with plenty of numerical examples. The making of ice-cream both on the small and large scales is fully treated, and chapters are added on the important and growing industries of the manufacture of milk sugar, casein, milk powders, and the preparation of fermented milks.

Service Chemistry. By VIVIAN B. LEWES, F.I.C., F.C.S., and J. S. S. BRAME, F.C.S. Fourth Edition. London: Edward Arnold. 1913.

THE importance of a knowledge of chemistry and metallurgy to naval and military officers is nowadays fully recognised, and the earlier editions of this book met with a well-deserved success which will undoubtedly be shared by the latest issue. The authors have kept the balance very well between the purely scientific side of the subject and the technical applications, and the discussion of every practical problem is led up to by a thorough explanation of the principles involved. The nature and causes of explosions and modern explosives are fully treated, and fuel problems, the corrosion of metals, the properties of alloys, boiler incrustations, and kindred subjects are discussed with special reference to the knowledge of them which the naval or military officer should possess.

The Journal of the Alchemical Society. Edited by H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S. Vol. I. Part 3. London: H. K. Lewis. 1913.

THE Alchemical Society was founded in 1912 for the study of the works and theories of the alchemists, and some interesting papers have been read before its meetings and subsequently published in the *Journal*. An ably written paper by Mr. Sijil Abdul-Ali on "An Interpretation of Alchemy in Relation to Modern Scientific Thought" is contained in No. 3 of the *Journal*, together with an abstract of the discussion which followed the reading of it before the Society.

Blue Book of Safety Appliances. London and Glasgow Messrs. Wallach Bros., Ltd.

THIS booklet contains fully illustrated particulars of the patent oxygen apparatus designed by Messrs. Wallach Bros., Ltd., as well as many different kinds of helmets, masks, and other safety appliances, first aid cabinets, &c. A copy of the memorandum by H.M. Chief Inspector of Factories as to the use of water gas and other gases in factories and a very favourable report by Mr. B. H. Thwaite, C.E., on the various appliances are reproduced.

Die Fabrikation der Tonerde. ("The Manufacture of Clay"). By Dr. phil. A. BERGE. Halle-a.-S.: Wilhelm Knapp. 1913. (M. 3.80).

THE great advances which have been made in recent years in methods of manufacturing clay are well described in this monograph, which is designed to meet the want which has for some time been felt for a concise handbook on the subject, which, while not entering into full details, gives a clear and adequate summary of modern developments of the industry. The preparation of clay from bauxite is naturally given special prominence, and the treatment of the raw material, the ignition process, extraction of melt, &c., are carefully described. A short account is given of the uses of clay, including fused clay and artificial gems, and the preparation of aluminium metal is very briefly treated.

CORRESPONDENCE.

HUMPHREY OWEN JONES MEMORIAL FUND.

To the Editor of the Chemical News.

Sir,—The Committee formed to carry out the generally expressed desire that some suitable memorial of the late Humphrey Owen Jones, F.R.S., should be established, has received subscriptions amounting to about £3600. It is proposed to devote the sum collected to the endowment of a teaching post in Physical Chemistry in the University of Cambridge.

The Committee desires to close the subscription list at the end of this month, and requests further intending subscribers to send their contributions to the account of the H. O. Jones Memorial Fund, Messrs. Barclay and Co.'s Bank, Cambridge, before that date.—I am, &c.,

William J. Pope,
Chairman of the Committee.

The Chemical Laboratory, Cambridge,
July 7, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 16, April 21, 1913.

Tetra-alkylation of Cyclohexanone and β-Methylcyclohexanone, and Tri-alkylation of Menthone.—A. Haller.—By the help of sodamide it is possible to replace all the atoms of hydrogen united to the two atoms of carbon attached to the CO group in a cyclohexanone (whether substituted or not) by hydrocarbon radicles. In the cases of the simple cyclic ketone and its β-methyl derivative condensation products are always formed, the latter condensing less easily than its lower homologue, while menthone gives no condensation products. With cyclohexanone itself this condensation becomes more marked when attempts are made to introduce homologous radicles superior to methyl, so that only very few substituted derivatives are obtained. The tetra-, penta-, and hexa-alkylcyclohexanones do not combine with either hydroxylamine or semicarbazide, and in ether, benzine, and toluene they resist the action of sodamide. In xylene they are split up, yielding very complex basic derivatives.

Thermic Study of Uranyl Nitrate and its Hydrates.—M. de Forcrand.—From the heat of solution of the hydrates of uranyl their boiling-points can be calculated. The hexahydrate appears to be a compound, the efflorescence tension of which is not negligible at the ordinary temperature and the crystals may contain a little less than $6H_2O$. The trihydrate is more stable, but the efflorescence tension is not quite negligible at the ordinary temperature. The dihydrate is still more stable, but at 98° it very slowly loses one of its molecules of water, while at 110° the other molecule is driven off after 150 hours.

Dissociation of Gaseous Compounds by Light.—Daniel Berthelot and Henry Gaudechon. — The law according to which in a given family of elements the stability of the compounds towards light decreases as the atomic weight increases is verified in the nitrogen and carbon families, as shown by the study of ammonia, phosphoretted hydrogen and arseniuretted hydrogen, and of methane and hydrogen silicide.

No. 17, April 28, 1913.

Methylation of Isovalerone by Sodamide and Methyl Iodide.—A. Haller and Edouard Bauer.—When sodamide and methyl iodide act on isovalerone the successive products are symmetrical dimethylisovalerone, trimethylisovalerone, and symmetrical tetramethylisovalerone. The last ketone yields neither oxime nor semicarbazone. When reduced with sodium and absolute alcohol it gives the corresponding alcohol.

Absorption of Neon by Electrodes of Luminescent Tubes.—Georges Claude.—If a luminescent tube is filled with neon containing 1 per cent of helium the latter is rapidly absorbed, and is found in an increased proportion in the gases disengaged from the volatilised metal. A small amount of neon present in an atmosphere of helium is not similarly eliminated. Nitrogen resembles helium in being much more readily absorbed than neon, and apparently the resistance of neon to absorption by electrodes is a true characteristic of this substance, which is also remarkable for its power of causing the cathodic volatilisation of certain metals and for its very feeble dielectric cohesion.

Density of Double Salts.—Ed. Chauvenet and G. Urbain.—From experiments performed with the double chlorides of copper and ammonium it appears that the following law may hold good in certain cases:—The molecular volume of a double salt is frequently equal to the sum of the molecular volumes of its constituents. Thus the molecular volume behaves like the other properties (colour, magnetism, chemical properties, &c.), with reference to which the salt in question appears to be a perfect double salt.

Quantitative Study of the Absorption of Ultra-violet Rays by Ketones, Diketones, and Ketonic Acids.—Jean Bielecki and Victor Henri.—All substances of formula $C_nH_{2n+1}COC_pH_{2p+1}$ possess an absorption band between 2700 and 2800, its position and height depending upon the values of n and p. The linking of the carbon atoms in the monoketones and the position of the ketonic group in the chain influence the absorption. When two ketonic groups are present in the same molecule an exaltation of the absorption band is observed, but the position of the maximum is not affected. If ketonic and carboxyllic groups are both present the absorption characteristic of the carboxyl group is raised and that of the carbonyl group is lowered. When a substance can exist in both the ketonic and enolic forms the absorption varies with the proportion of the two forms present.

Action of Formic Acid on Triphenylmethane Dyes.—A. Guyot and A. Kovache.—When formic acid acts on triphenylmethane dyes normal reduction first takes place, but the leucobase formed is ultimately reduced and split up. There is evidently a complete continuity between the dyes and the carbinols deprived of all auxochrome, and the only difference between the two groups of compounds lies in their reactive power, which depends upon the basicity of the molecules.

No. 19, May 31, 1913.

Preparation of Dicyclohexylbutanes.—Paul Sabatier and M. Murat.—Theoretically there should be nine isomeric dicyclohexylbutanes, six derived from normal and three from isobutane. None of these have been known before, but the authors have now prepared five of them (three from normal butane) by the direct hydrogenation of the corresponding hydrocarbons in presence of nickel. Thus from symmetrical diphenylbutane 1 . 4-dicyclohexylbutane is obtained, and from 1 . 2-diphenylbutane 1 . 2 dicyclohexylbutane.

Degradation of Mono and Dibasic Saturated Acids.—Th. Barbier and R. Locquin.—Lower homologues can be obtained from the saturated acids by first transforming the carboxyl into a tertiary alcohol group by the action of two molecules of CH_3MgI on the ethyl or methyl ether:—

$$R.CH_2.CO.OCH_3 + 2CH_3MgI \rightarrow R-CH_2-C(OH)<^{CH_3}_{CH_3}.$$

Then the tertiary alcohols or the unsaturated hydrocarbons derived from them by dehydration are oxidised:—

$$RCH_2COH<^{CH_3}_{CH_3} + O_3 = R.COOH + CH_3.CO.CH_3 + H_2O.$$

The ketones can be used for this transformation instead of the ether salts. If the COOH group is attached to a CH_2 the group $\begin{matrix}CH_3\\CH_3\end{matrix}>OH$ is eliminated as $CH_3.CO.CH_3$, while the neighbouring CH_2 is transformed into COOH. This the initial acid is converted into its next lower homologue. When the COOH is attached to a substituted carbon atom the principal product of oxidation is a ketone. The dibasic acids behave like the monobasic acids, both carboxyl groups being attacked.

Solid Phosphides of Hydrogen.—Louis Hackspill.—When the alkaline phosphides of formula P_5M_2 are treated with hydrochloric acid or acetic acid (very dilute), a yellow phosphoretted hydrogen of formula P_5H_2 is obtained. The existence of P_2H or $P_{12}H_6$ seems doubtful. The author, in collaboration with M. R. Bossuet, has obtained a series of metallic phosphides corresponding to the acid P_5H_2.

Phenyl-α-oxycrotonic Acid.—J. Bougault.—Good yields of phenyl-α-oxycrotonic acid can be obtained by saponifying the amide with oxalic acid. In the course of his researches on the preparation of phenyl-α-oxycrotonic acid the author has obtained an acid of formula $C_{10}H_{10}O_3$, which results from a new isomerisation of the original acid. It appears to be $C_6H.COH=CH.CH_2.CO_2H$, and is thus the enol form of benzoylpropionic acid into which it is transformed by caustic alkalis and strong acids. It is a crystalline substance fusing at 91°.

1-Benzoyl-2-Phenyl-Δ_2-Cyclopentene.—Edouard Bauer.—Sodamide brings about the condensation and cyclisation of dibenzoylbutane, giving 1-benzoyl-2-phenyl-Δ_1 cyclopentene fusing at 53°, and its Δ_2 isomer fusing at 98°. The latter gives with sodamide a derivative which reacts with alcoholic iodides with formation of an alkyl ketone, which reacts with sodamide like a trialkylacetophenone. In this reaction the carbon chain is broken at the CO group, with formation of 1-methyl-2-phenyl-Δ_2-cyclopentene and benzoic amide or of benzene and the amide of 1-methyl-2-phenyl-Δ_2-cyclopentene-1-carboxylic acid.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 9, 1913.

Uranyl Formate.—Gaston Courtois.—When a concentrated aqueous solution of uranic acid crystallises with formic acid only one hydrate is formed at the ordinary temperature, the neutral formate, $(HCO_2)_2UO_2.H_2O$. When dried over sulphuric acid this hydrate is very stable up to 100°; when the temperature is raised it gives up water up to 150° and then very slowly decomposes. In concentrated aqueous solution the salt decomposes with formation of a basic crystallised salt of formula $(HCO_2)_2UO_2.H_2O.NO_3.3H_2O$. This basic salt is decomposed by prolonged boiling, giving finally uranic acid, UO_3H_2O. The properties of the author's salt are very different from those attributed by Oechsner de Coninck and Raynaud to uranyl formate.

Zirconium Carbonates.—Ed. Chauvenet.—Zirconium oxide combines with carbonic acid to give hydrated orthocarbonates, neutral and basic. When these compounds are heated they are converted into more and more basic and hydrated derivatives, but no anhydrous carbonate is obtained, and apparently no anhydrous carbonate, either neutral or basic, can exist.

Benzoyl Cyanhydrines, Benzoyl-amides of Aldehydes, and the Corresponding Acid Alcohols.—M. Aloy and Ch. Rabaut.—The cyanhydrines of formic, propyl, and isobutyl aldehydes can be prepared by allowing a molecule of benzoyl chloride to act on an equimolecular mixture of the aldehyde and potassium cyanide in aqueous solution. In contact with concentrated HCl the cyanhydrines readily yield the corresponding amides from which the acids are obtained by saponification. The benzoyl cyanhydrine of furfurol can be obtained similarly, but it does not give an amide or acid.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 7.

Behaviour of Hydrogen towards Palladium.—A. Gutbier, H. Gebhardt, and Berta Oltenstein.—In agreement with the results of Paal and Amberger the authors have found that as the temperature is lowered there is a very considerable increase in the amount of hydrogen occluded by palladium. At +20° the minimum occlusion occurs. The preparations of hydrogen-palladium obtained are pyrophoric.

Action of Alkali Arsenite on Ethyl-disulphide.—A. Gutmann.—Ethyl disulphide acts on tertiary sodium arsenite in the cold, giving sodium arsenate and ethyl mercaptan. This oxidising action is remarkable, since the disulphide contains no oxygen, but it is evidently due to the peroxide character of the disulphide; it acts upon water, removing hydrogen and liberating oxygen:—

$$\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}+H_2O=2C_2H_5.SH+O,$$

and the oxygen then converts the arsenite into arsenate.

Stable Chromous Oxide Compounds.—Wilhelm Traube and W. Passarge.—Certain chromous oxide salts form with free hydrazine stable salts which still contain divalent chromium, but unlike other chromous salts are quite stable in air. They can be exposed to atmospheric oxygen for a day without undergoing any change, and some of them are not even oxidised when suspended in water. If, however, they are dissolved in acids or in ammonia they readily absorb oxygen from the air. The following chromous hydrazine salts have been prepared:—$CrCl_2.2N_2H_4$, $CrBr_2.2N_2H_4$, $CrI_2.2N_2H_4$, and $CrSO_4.(N_2H_4)_2.H_2SO_4$.

Anhydrous Chlorides of Iridium of Four Different Valencies.—Lothar Wöhler and S. Streicher.—The formation of anhydrous $IrCl_4$ occurs very slowly below 100° from trichloride and chlorine under high pressure. The complex H_2IrCl_6 loses HCl above 100°, yielding chlorine with a higher pressure than 1 atmosphere. The trichloride can very easily be prepared from the metal and chlorine at 600°. In chlorine, at a pressure of 1 atmosphere, the trichloride can exist at temperatures ranging from 763° to 100°. The chlorination of the metal and the dissociation of the trichloride in certain conditions may lead to the formation of a dichloride or a monochloride. The former is capable of existence only between 763° and 773°, and the latter between 773° and 798° in an atmosphere of chlorine.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [1.], No. 5, 1913.

Notes on the Constitution of the Azoxy Compounds.—Angelo Angeli.—When an azo compound, $C_6H_5N=N.C_6H_5$, is treated with bromine or nitric acid the bromine atom or nitric radical takes up the para position in the $N.C_6H_5$ residue, probably with the intermediate formation of a dibromide:—

$$=N.C_6H_5+Br_2\rightarrow\ =N.C_6H_5(Br_2)\rightarrow\ =N.C_6H_4Br+HBr.$$

Ordinary azoxybenzene gives a dibromide which readily loses HBr, forming a parabromo derivative. Thus α-parabromoazoxy benzene is probably $C_6H_5.N=N.C_6H_5$ (O) and the β-compound is $C_6H_5.N=N.C_6H_5$ (O). The α derivative with bromine gives a dibromo derivative identical with that obtained by the action of hydrogen peroxide on paradibromoazobenzene. Apparently the atom of oxygen protects the aromatic residue united to the same nitrogen atom from the action of the substituent.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2799.

SOLUBILITIES OF THE RARE EARTH SALTS OF BROMO-NITRO-BENZENE-SULPHONIC ACID (1 : 4 : 2).*

By S. H. KATZ and C. JAMES.

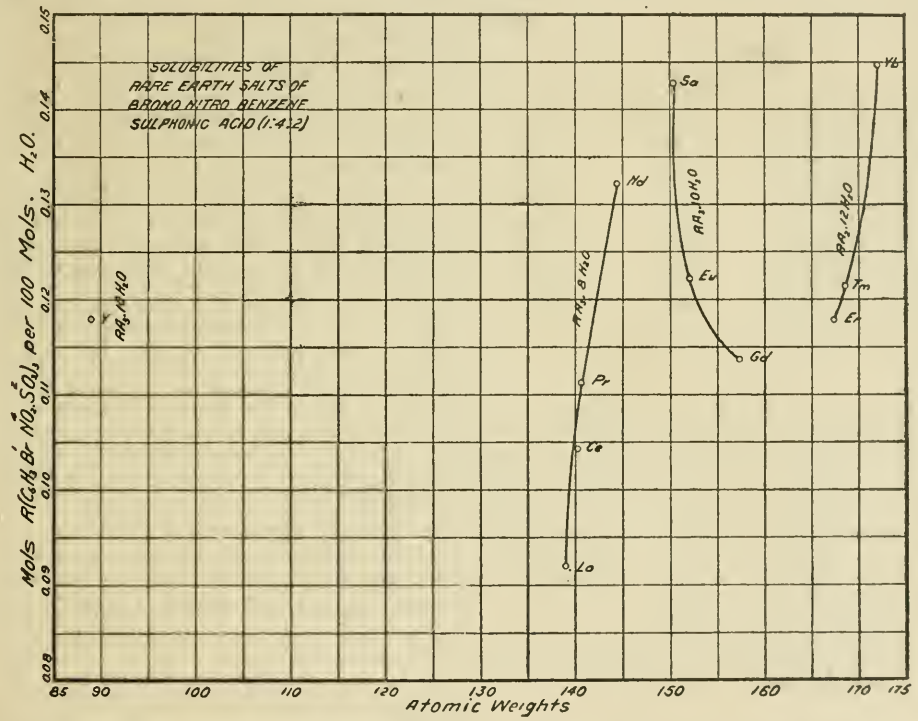
Holmberg (*Chem. Centr.*, 1906, ii., 1595) used meta-nitro-benzene sulphonic acid very successfully for the separation and purification of neodymium. Derivatives of this acid therefore gave promise of being useful in work on the rare earths.

Bromo-nitro-benzene sulphonic acid (1 : 2 : 4) was prepared by the method of Limprecht (*Ber.*, viii., 456). The lanthanum, cerium, and yttrium salts of this acid were prepared and found to be very soluble. By spontaneous evaporation yellow warty crusts finally formed, which were useless for crystallising.

Bromo-nitro-benzene-sulphonic acid (1 : 4 : 2) was prepared by the method of Augustin and Post (*Ber.*, viii., 1559). In sulphonating the bromo-nitro-benzene it was treated with two and one-half times its weight of sulphuric acid containing 40 per cent free SO_3 at 100°, until the mixture dissolved completely in water, which required about twenty-four hours. The product was treated with $BaCO_3$ and excess of soluble barium then removed by treating with the proper amount of H_2SO_4. Considerable other acid material besides the bromo-nitro-benzene-sulphonic acid (1 : 4 : 2) was formed. The latter crystallised well from a boiling, saturated, aqueous solution. A pure material was obtained by a series of fractional crystallisations of the crude acids. The yield was about 30 per cent. Salts of lanthanum, cerium, yttrium, and ytterbium were prepared. All crystallised nicely from solution, forming salts only very faintly tinged with the yellow colour of the acid. The properties were such that this acid was seen to offer opportunity for a definite comparative study of the properties and solubilities of a series of rare earth salts.

The compounds of the acid with yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, thulium, and ytterbium were prepared and crystallised from solution. The first crop of crystals only were used in this work.

Composition was found by determination of water of crystallisation by heating the air dry crystals to 200°, and by determination of R_2O_3 by means of the oxalate precipitation and ignition. In the case of praseodymium the oxalate was titrated with a standard $KMnO_4$ solution. The results are given in Table I.



In the case of the erbium, thulium, and ytterbium compounds, which contained twelve molecules of water of crystallisation, the water could not be determined, because at the temperature used for the other salts these were charred, while at a lower temperature the water was not all evolved.

The colours of the salts of praseodymium, neodymium, samarium, erbium, and thulium were not modified noticeably by the colour of the acid radical. The compounds containing eight molecules of water of crystallisation formed needle-like crystals; those containing ten molecules, thin orthorhombic plates, and those containing twelve molecules less regular plates and needles.

The solubilities were determined after allowing equilibrium to become adjusted by rotation in a thermostat

* Contribution from the Chemical Laboratory of New Hampshire College.

TABLE I.

		H_2O (per cent). Cal.	H_2O (per cent). Found.	R_2O_3 (per cent). Cal.	R_2O_3 (per cent). Found.
Y	$(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	16·29	15·90 15·98	10·16	10·13 10·07
La	$(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·80	12·80 12·90	14·46	14·41 14·38
Ce	$(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·78	12·60 12·60	14·58	14·50 14·58
Pr	$(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·78	13·05 12·78	14·59	14·40 14·43
Nd	$(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·74	12·82 12·66	14·88	14·79 14·82
Sa	$(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·35	15·01 14·96	14·86	14·90 14·90
Eu	$(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·34	14·98 15·33	14·91	14·83 14·98
Gd	$(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·27	14·93 14·99	15·36	15·43 15·47
Er	$(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·60	15·62 15·62
Tm	$(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·68	15·64 15·43
Yb	$(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·96	15·95 16·02

TABLE II.

		Mols. anhydrous salt per 100 mols. H_2O.	Per cent anhydrous salt.
Y	$(C_6H_3Br.NO_2.SO_3)_3$	0·1178	5·739
La	$(C_6H_3Br.NO_2.SO_3)_3$	0·09207	4·771
Ce	$(C_6H_3Br.NO_2.SO_3)_3$	0·1043	5·559
Pr	$(C_6H_3Br.NO_2.SO_3)_3$	0·1112	5·730
Nd	$(C_6H_3Br.NO_2.SO_3)_3$	0·1322	6·762
Sa	$(C_6H_3Br.NO_2.SO_3)_3$	0·1427	7·272
Eu	$(C_6H_3Br.NO_2.SO_3)_3$	0·1222	6·310
Gd	$(C_6H_3Br.NO_2.SO_3)_3$	0·1137	5·938
Er	$(C_6H_3Br.NO_2.SO_3)_3$	0·1178	6·056
Tm	$(C_6H_3Br.NO_2.SO_3)_3$	0·1214	6·379
Yb	$(C_6H_3Br.NO_2.SO_3)_3$	0·1397	7·294

kept constant at 25°. The results in Table II. are averages of duplicates.

The solubilities plotted against atomic weights are shown graphically in the accompanying diagram. It is seen that, with change in the water of hydration, there is a change in direction of the solubility curve, which amounts to a reversal of the slope. The phenomenon shown may be compared to that producing the change in the general direction of the temperature-solubility curve of a single salt forming various molecular compounds with water at different temperatures. That is, with a break in the general direction of the solubility curve there is a change in the nature of the compound.

Work on the separation of various rare earths by crystallising salts of bromo-nitro-benzene sulphonic acid (1 : 4 : 2) is now under way in this laboratory.

Durham, N.H.

Two Characteristic Colour Reactions of Phenylalanine.—L. Chelle.—To identify phenylalanine a little of the substance is dissolved in 4 cc. of H_2SO_4 in the cold and the solution is divided into two portions. One drop of formol is added to the one, when an orange colouration, rapidly turning brown, is produced. One drop of an alcoholic solution of paraldehyde is added to the other, and after ten minutes a lemon colouration is produced. After an hour it exhibits a green fluorescence. By these two reactions one milligrm. of phenylalanine can be detected. The second test is most useful for quantitative determination, which can be performed by comparing the colourations obtained after one hour.—*Bulletin des Travaux de la Société de Pharmacie de Bordeaux*, vol. liii., March, 1913.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER.*

NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION.

By J. SAM GUY, E. J. SHAEFFER, and HARRY C. JONES

THE use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy (*Phys. Zeit.*, 1912, xiii., 649). The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate, because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensity. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave-lengths than the photographic method.

In building a radiomicrometer that would be adapted to this work, that is, with sufficient sensibility and with a short period, one of the greatest difficulties encountered was to obtain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds and Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermoelectric junction already described (*Phys. Zeit.*, 1912, xiii., 651), a most sensitive radiomicrometer which at the same time had a very short period was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the *Physikalische Zeitschrift*, was done with this instrument.

At the beginning of the present academic year the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less*, and in some cases *very much less*, than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light, the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has very different absorption from an equal amount of pure uncombined water.

We then carried out a number of experiments in cells whose depths could be easily and accurately adjusted, with different substances, in the following manner:—We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission, that is, the deflection of the radio-

* This investigation was carried out with the aid of a Grant generously awarded by the Carnegie Institution of Washington to H C. Jones. From the *American Chemical Journal*, xlix., No. 4.

micrometer for the solution, divided by the deflection for water, for the first named substances amounted to more than 100 per cent. Pure water had a different absorption from an equal depth of water in the solution, and since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated are more transparent than pure water having the depths of the water in the solutions in question. Solutions of non-hydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure uncombined water. To test this quantitatively the following procedure was adopted :—

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of, say, 21 mm. Some of the same solution was then placed in another cell set to a depth of, say, 1 mm. Light of given known wave-length was then passed through the one solution and the deflection noted. Light of this same wave-length was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave-length of light from reading to reading by only a small amount. Light of any given wave-length was always passed through the one solution, and then at once through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say, 20 mm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave-length of light, and then, at once, the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave-lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in uestion.

Table I.

	4/N KCl.		4/N NH_4Cl.		3·12/N NH_4NO_3.	
λ.	I/I_0.	H_2O.	I/I_0.	H_2O.	I/I_0.	H_2O.
710	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58	58	59
979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43
1007	39	43	41	42	39	44
1013	40	42	39	44	41	44
1019	42	46	40	46	42	44
1025	41	42	44	49	45	48
1032	49	49	44	49	48	49
1037	53	52	56	55	52	53
1042	56	56	53	58	55	55
1046	59	60	57	57	57	60
1059	63	62	58	65	60	65
1065	68	67	62	67	64	65
1072	71	68	64	68	66	69
1078	74	72	67	67	66	72
1085	75	73	67	66	68	74
1100	77	75	68	72	69	78
1113	76	76	69	72	69	78
1138	75	72	68	70	68	72
1148	70	69	64	65	64	71
1158	64	63	62	64	59	64
1165	58	59	58	58	56	60
1172	52	51	50	50	53	52
1179	42	40	40	40	38	41
1186	29	28	29	26	29	30
1193	18	19	19	19	18	19
1200	13	16	14	13	12	17
1206	10	12	12	12	9	13
1213	10	11	10	12	9	13
1220	10	11	10	11	9	12
1227	10	11	10	11	9	12

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave-lengths being abscissæ and transmission ordinates. A comparison of the two curves shows at once whether water in the free uncombined condition or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colourless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

TABLE II.

λ.	4/N KCl. I/I_0.	H_2O.	4/N NH_4Cl. I/I_0	H_2O.	3·12/N NH_4NO_3. I/I_0.	H_2O.
1085	85	86	79	87	81	88
1100	87	88	80	92	81	93
1113	86	87	79	86	84	86
1138	81	85	79	84	81	84
1148	79	82	77	84	78	84
1158	80	79	74	81	76	81
1165	76	77	71	77	72	77
1172	72	71	66	70	67	70
1179	64	62	59	62	61	62
1186	51	51	52	50	50	50
1193	41	43	42	44	40	44
1200	35	38	37	40	34	40
1206	37	36	35	37	32	37
1213	30	34	30	36	32	36
1220	30	35	29	35	34	35
1227	30	34	30	35	32	35
1233	30	33	28	35	31	35
1241	30	34	29	34	31	34
1248	31	34	28	33	31	33
1250	33	34	30	34	32	34
1255	34	35	30	36	32	36
1268	34	35	31	37	32	37
1270	37	31	32	38	33	38
1285	38	38	33	38	33	38
1295	39	38	32	38	33	38
1300	41	38	32	39	34	39
1308	42	39	32	41	35	41
1316	41	39	32	40	34	40
1323	42	37	32	38	34	38
1330	40	37	32	37	33	37
1338	40	35	30	35	31	35
1346	36	33	28	36	30	36
1352	34	29	26	29	27	29
1358	29	26	23	27	25	27
1365	25	22	21	23	21	23
1372	20	18	17	20	17	20
1387	13	12	12	11	10	11
1404	7	7	7	8	7	8
1418	3	4	4	3	3	3
1430	2	2	3	2	2	2
1445	0	0	0	1	1	1

TABLE III.

λ.	5·38/N $CaCl_2$. I/I_0.	H_2O.	4·96/N $MgCl_2$. I/I_0.	H_2O.	1·2/N $Al_2(SO_4)_3$. I/I_0.	H_2O.
710	94	98	95	98	95	93
724	92	98	98	98	95	95
741	90	95	95	98	94	93
760	87	94	94	98	92	93
776	88	93	92	97	93	95
798	91	96	93	94	92	90
818	93	99	90	90	93	92
836	92	97	92	95	92	92
855	90	93	91	90	90	91
878	90	90	91	93	91	90
900	89	92	88	92	89	90
922	86	91	88	91	85	86
947	87	84	84	86	82	81
958	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1007	42	46	46	48	46	38
1013	42	46	45	50	46	39
1019	43	49	44	51	44	40
1025	47	50	46	44	46	43
1032	52	53	51	54	46	45
1037	55	55	52	56	52	50
1042	58	59	56	58	53	53
1046	62	62	59	65	55	55
1059	66	65	63	67	55	58
1065	71	70	69	70	62	63
1072	74	72	71	75	60	65
1078	75	74	71	76	64	69
1085	78	76	76	79	65	70
1100	80	77	78	79	67	72
1113	79	78	80	81	67	74
1138	77	75	77	78	64	67
1148	74	71	75	77	60	65
1158	69	65	73	73	57	55
1165	66	62	65	65	55	53
1172	61	52	61	58	50	43
1179	54	41	52	44	45	34
1186	42	30	43	32	34	22
1193	32	21	32	24	25	15
1200	22	17	23	18	20	12
1206	16	16	18	17	16	10
1213	13	15	16	18	14	9
1220	12	13	14	15	11	10
1227	12	13	14	16	12	8

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride, and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layers of each solution of every substance investigated were employed. The object of this was to bring out the two most important water bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water bands would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above, that is, by the differential method, we were able to investigate both of the water bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

In the accompanying tables, under λ are given the wave-lengths of light that were passed through the solution, and under I/I_0 the percentage of transmission, on the one hand, of the solution, and, on the other, of water having a depth exactly equal to that of the water in the solution.

The ordinates of the curve, as has already been state , are percentage transmissions and the abscissæ wave-lengths.

In Table I. the depth of layer of all the solutions was the difference between 21 and 1, *i.e.*, 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the solutions in Table II. was the difference between 11 mm. and 1 mm., *i.e.*, 10 mm. The depth of water used was in every case the same as that of the water in the solution.

In Table II. the depth of layer of the solution that was used was only half of that in Table I. The object of this was to bring out more prominently the second water band.

The depth of later of the solutions in Table III. was the difference between 21 mm. and 1 mm., *i.e.*, 20 mm. The depth of water used in every case was the same as that of the water in the solution.

In Table IV. the depth of layer used was the difference between 11 and 1 mm., *i.e.*, 10 mm. The object of using the smaller depth of the solution was to bring out more clearly in the case of hydrated salts the second water band.

Table IV.

λ.	5·38/N $CaCl_2$. I/I₀.	H_2O.	4·96/N $MgCl_2$. I/I₀.	H_2O.	1·02/N $Al_2(SO_4)_3$. I/I₀.	H_2O.
1085	84	84	82	84	79	82
1100	84	84	83	84	78	81
1113	84	86	83	84	78	84
1138	86	85	82	83	77	83
1148	82	83	79	80	75	80
1158	80	79	77	77	73	77
1165	78	76	77	75	70	73
1172	76	72	74	70	66	69
1179	72	65	71	64	63	58
1186	63	55	62	52	55	48
1193	54	45	56	46	49	39
1200	45	40	48	42	43	34
1206	38	39	42	40	38	30
1213	35	39	39	38	36	29
1220	33	36	37	38	34	28
1227	32	36	36	38	32	28
1233	31	35	34	37	32	28
1241	32	35	34	34	31	28
1248	32	35	34	37	31	28
1250	33	35	34	38	31	28
1255	33	37	34	38	31	28
1268	35	38	33	38	30	29
1270	37	39	34	39	30	30
1285	38	40	35	40	30	31
1295	40	40	35	40	30	32
1300	42	41	36	41	30	32
1308	42	41	37	42	30	33
1316	45	41	39	42	30	33
1323	47	40	39	41	28	33
1330	46	39	40	40	27	32
1338	45	37	38	38	27	30
1346	42	35	38	36	24	27
1352	40	32	34	33	22	24
1358	37	29	33	30	20	21
1365	33	25	29	26	18	19
1372	29	21	25	22	15	15
1387	19	13	18	15	10	9
1404	12	10	12	11	7	5
1418	7	6	7	9	4	3
1430	3	3	4	3	2	2
1445	2	1	1	1	1	1

(To be continued)

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

Sugar may Stop the Development of Young Subjects.

MM. Jacques Parisot and Pierre Mathieu have arrived at the following conclusions after having subjected a certain number of rabbits to the ingestion of sugar for periods varying from a few weeks to several months :—

At first a decrease of weight is observed, soon followed by a recovery or even an increase, then finally a persistent decrease. The troubles caused by the first ingestions are pretty easily reparable, those resulting from the absorption of abundant and repeated doses are much more lasting. Lastly, the animals experimented upon feel indefinitely the effects of this obstacle thus opposed to their development.

These are but laboratory experiments, effected on animals, and their results, naturally, could not, uncontrolled, be applied to human beings. Nevertheless, they are worth taking into consideration, and it would be advisable to have but a limited confidence in the alimentary value of sugar whenever it is absorbed in considerable quantities.

The Watering of the Land.

It is well known how much the watering of the ground increases the production of the crops as well as the value of the land. Generally water only exists in insufficient quantities, and it is necessary not to waste it, so as to make it go over as large a space as possible.

In their studies MM. Mintz and Lainé have discovered that generally too much water is employed, and that it might be economised without diminishing the effects of irrigation. This water might then be employed over larger surfaces.

The two chemists have determined the quantities of water really useful for grounds of different kinds. These quantities vary enormously. MM. Mintz and Lainé have also fixed the data of a rational arrangement which would realise a great economy of water.

Extraction of Oil from Condensation Water.

The escapement vapour of steam engines draws off, mechanically with itself, the greasing oil, and this has induced engineers to construct different apparatus for the extraction of this oil. But ordinary separators only retain about 75 per cent ; the 25 per cent which remains go into the condenser, where they produce in the water little spheric corpuscles, a veritable emulsion as it were, which forms a layer on the surface of the water. This layer presents the particularity of being electrically charged and acts like a veritable colloidal solution.

It is then possible by the addition of a colloidal solution, charged with electricity of a contrary sign, to produce the precipitation of the oil. This is what takes place in a new process that consists in electrolysing the water by the help of electrodes of iron after having rendered it conductive by a dissolution of carbonate of soda.

It is thus possible to eliminate 98·5 per cent of the oil, and the expense for the electric current and the carbonate of soda does not exceed five centimes (one half-penny) per cubic metre treated. Moreover, the small quantity of alkali that remains in the water is advantageous, as it has the effect of delaying the attack on the iron of the walls of the cauldron.

The Forecast of Storms by Wireless Telegraphy.

M. Turpain, Professor at the Faculty of Science of the University of Poitiers, continues to pursue his experiments concerning the forecast of storms by wireless telegraphy.

The observations, registrations, and forecasts of storms have, says M. Turpain, been pursued throughout the year 1912 by means of different arrangements of apparatus that I described last year, principally by means of receptive apparatus with needles, inserted in the circuit of an enregistrating milli-ampèremeter. These apparatus have been worked at the posts of Poitiers (Faculty of Sciences, Manroc, University of Poitiers), La Rochelle, Paris-la-Nation, the Observatory of the Pic du Midi, Bagnères de Bigorre, the Observatory of the Puy de Dôme.

The forecast was currently from four to five hours, and sometimes reached six to eight hours.

The station installed in Paris, Place de la Nation, has been able to warn the farmers of Montreuil and to avoid them having firing to prevent hail storms, either when the weather although threatening was not stormy, or when it was deduced from the inscription that the storm would not pass over Montreuil. In this way, with a saving of L. 8 for every firing avoided, the Paris station was able to make the Montreuil part economise several thousand francs.

The same apparatus are employed at the Bordeaux Observatory for the control of the para-hail apparatus installed in the department of Gironde.

Besides these indications of a practical order, the indications supplied by the foretellers allow of great precision in the meteorological data. Thus, at the Observatory of Bagnères de Bigorre most valuable information has been deduced concerning the prevision of the weather. At Paris-la-Nation stormy weather has been foretold successfully several times thirty-four hours in advance.

The studies made with a view of foreseeing rain or a rainy period have been pursued, and have given a concordance of about 75 per 100. These researches are especially to be pursued with bolometric apparatus allowing of the enregistering of the energy of the discharges. In order to confirm these new results it is necessary to undertake new bolometric measures simultaneously in two posts of observation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 26th, 1913.

Sir RONALD ROSS, K.C.B., Vice-President, in the Chair.

PAPERS were read as follows:—

"*Phosphorescence of Mercury Vapour after Removal of the Exciting Light.*" By F. S. PHILLIPS.

"*Light Sensations and the Theory of Forced Vibrations.*" By Dr. G. J. BURCH, F.R.S.

"*Fluctuation in the Ionisation due to γ-Rays.*" By P. W. BURBIDGE.

"*Force Exerted on a Magnetic Particle by a varying Electric Field.*" By J. G. LEATHEM, M.A.

"*Luminosity Curve of a Colour Blind Observer.*" By W. WATSON, F.R.S.

"*A Critical Study of Spectral Series.* Part III. *The Atomic Weight Term, and its Import in the Constitution of Spectra.*" By Prof. W. M. HICKS, F.R.S.

"*A Band Spectrum Attributed to Carbon Monosulphide.*" By L. C. MARTIN.

A complex band system occurring in the spectrum of the electric discharge through carbon disulphide vapour in addition to the bands due to sulphur, is also found in the spectrum given by sulphur in the carbon arc. These bands only occur in the presence of both sulphur and carbon, and are probably due to carbon monosulphide.

"*Structure of the Skull of Dicynodon as Revealed by Serial Sections.*" By IGERNA B. J. SOLLAS and W. J. SOLLAS, F.R.S.

"*Carbohydrate-metabolism in its Relation to the Thyroia Gland.—The Effect of Thyroid Feeding on the Glycogen Content of the Liver and on the Nitrogen Distribution in the Urine.*" By W. CRAMER and R. A. KRAUSE.

"*Sublimation of Metals at Low Pressures.*" By G. W. C. KAYE, D.Sc., and D. EWEN.

"*Energy of Röntgen Rays.*" By R. T. BEATTY, D.Sc.

"*Some Phenomena of Sunspots and of Terrestrial Magnetism.*" Part II. By Dr. C. CHREE, Sc.D., LL.D., F.R.S.

The paper is a continuation of one termed for brevity S.M., which appeared in the *Phil. Trans.*, A, ccxii., 75. It is mainly devoted to the question of the existence of a period of approximately twenty-seven days in terrestrial magnetic phenomena. Independent studies of magnetic storms during a very long period of years at Greenwich and Toronto led Mr. Harvey and Mr. Maunder a good many years ago to the conclusion that an interval of about twenty-seven and a-quarter days could be recognised between the commencements of successive magnetic storms in a greater number of cases than could reasonably be ascribed to pure chance. S.M. showed that whether one took the daily range of horizontal force at Kew, or the magnetic character of the day, there undoubtedly existed for the epoch 1890 to 1900 a period of twenty-seven days or slightly more, in the sense that if an individual day were highly or moderately disturbed, days twenty-seven or twenty-eight days later were on the average more disturbed than usual. The result was not peculiar to the large disturbance usually termed "magnetic storms," and appeared in all the years examined, whether quiet or disturbed.

The present paper finds the same result to hold true of the years 1906 to 1911 when use is made of the magnetic "character" figures which have been published since 1906 at de Bilt, under international auspices. It is also found that the result is as true of quiet as of disturbed characteristics. If an individual day is quiet, the day which is twenty-seven or twenty-eight days subsequent is on the average more quiet than normal. Moreover, whether the selected day is quiet or disturbed, the days which are earlier by twenty-seven or twenty-eight days show a relation to it exactly similar in character and amount to that shown by the day which is twenty-seven or twenty-eight days subsequent. The relation can also be traced both backwards and forwards in time for several successive multiples of the twenty-seven-day period, the amplitude of the successive "pulses" gradually diminishing.

The paper also investigates whether the phenomena presented by the twenty-seven day period vary with the period of the year, and what the relationships are, if any, between magnetic "character" and Greenwich measures of sunspot area and faculæ and Wolfer's sunspot frequencies. The apparent sunspot relationships are found to vary a good deal from year to year.

"*New Series of Lines in the Spark Spectrum of Magnesium.*" By A. FOWLER, F.R.S.

From experiments on the spectrum of the magnesium arc *in vacuo*, it has been found that there are seven lines which are associated with the well-known spark line 4481·35, their wave-lengths being 3104·91, 2661·00, 2449·68, 2329·68, 2253·94, 2202·75, and 2166·35. The eight lines, taken alternately, fall into two series having their common limit at 49776 on the frequency scale. The series are analogous to the two principal series of hydrogen lines, which have recently been investigated by the author.

"*Additional Triplets and other Series Lines in the Spectrum of Magnesium.*" By A. FOWLER, F.R.S., and W. H. REYNOLDS, B.Sc.

The paper gives particulars of eight new triplets which have been photographed in the ultra-violet spectrum of magnesium, and improved wave-lengths for some of the lines previously recorded. The Rydberg series of single lines has also been extended, and four strong solar lines of previously unknown origin have been identified with lines of this series. Attention is also drawn to a probable second subordinate series of single lines. Formulæ representing the various series are given.

"*A New Band Spectrum Associated with Helium.*" By W. E. CURTIS, B.Sc.

The paper describes a new band spectrum observed under certain conditions in vacuum tubes containing helium and hydrogen. The experiments suggest that the bands are due to helium, but until hydrogen can be more completely eliminated their origin cannot be regarded as definitely settled.

"*A Case of Abnormal Trichromatic Colour Vision Due to a Shift in the Spectrum of the Green Sensation Curve.*" Sir W. DE W. ABNEY, F.R.S., and W. WATSON, F.R.S.

"*Studies on the Processes Operative in Solutions (XXX.) and on Enzyme Action (XX.). The Nature of Enzymes and of their Action as Hydrolytic Agents.*" By E. F. ARMSTRONG and Prof. H. E. ARMSTRONG, F.R.S.

"*Studies on Enzyme Action.*" XXI. *Lipase.*" III. By Prof. H. E. Armstrong, F.R.S., and H. W. Gosney, B.Sc.

"*Studies in the Heat Production Associated with Muscular Work.*" (Preliminary Communication). By Prof. J. S. Macdonald.

"*Formation of the Anthocyan Pigments of Plants.*" Part VI. By Prof. F. Keeble, F.R.S., E. F. Armstrong, D.Sc., and W. N. Jones.

"*Question of Fractional Activity* ('*All or None*' *Phenomenon*) *in Mammalian Reflex Phenomena.*" By T. Graham Brown.

"*Thermal Effects Produced by Heating and Cooling Palladium in Hydrogen.*" By J. H. Andrew and A. Holt, D.Sc.

"*Peculiar Form of Low Potential Discharge in the Highest Vacua.*" By Hon. R. J. Strutt, F.R.S.

"*Note on Copying Machinery.*" By A. Mallock, F.R.S.

"*Relation between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution.*" Part II. By Walter Wahl.

"*Experiments on the Temperature Coefficient of a Kew Collimator Magnet.*" By G. A. Shakespear.

"*Spectroscopic Investigations in Connection with the Active Modification of Nitrogen.* III. *Spectra Developed by the Tetrachlorides of Silicon and Titanium.*" By W. Jevons.

"*Passage of Waves through Fine Slits in thin Opaque Screens.*" By Lord Rayleigh, O.M., F.R.S.

"*Reflection of X-rays by Crystals.*" II. By Prof. W. H. Bragg, F.R.S.

In a previous communication (April, 1913) it was shown that the wave-lengths of homogeneous pencils of X-rays could be expressed accurately in terms of the space relations of a crystal. The formula $\lambda = 2d \sin \theta$ connected the wave-length λ with θ, the glancing angle at which the pencil was reflected in the crystal face, and d the distance between parallel reflecting planes. The angle θ could be determined with accuracy, but want of exact knowledge of crystal structure threw difficulties in the way of a complete evaluation of wave-length. W. L. Bragg, using two independent methods of research (those of the Lane diagram, and of reflection in the crystal face), has shown that in all probability the value of d is $2{\cdot}81 \times 10^{-8}$ cm. From this it follows that the wave-length of the "B peak" is $1{\cdot}10 \times 10^{-8}$. Characteristic radiations having wave-lengths $1{\cdot}25 \times 10^{-8}$ and $1{\cdot}66 \times 10^{-8}$ are emitted by bulbs having anticathodes of tungsten and nickel respectively. So far as it has been found possible to measure the absorption coefficients, they belong to rays which are characteristic of the anticathode metals, and the quantum energy—Planck's constant multiplied by frequency—agrees well with the energy of the cathode ray which, according to Whiddington, is required to excite the X-ray, or which the X-ray can excite.

"*Structure of some Crystals as Indicated by their Diffraction of X-rays.*" By W. L. Bragg.

An analysis of the Lane diagram of sylvine (KCl) shows that the diffracting centres are arranged on a space lattice of the simplest cubicle form. The diagrams of potassium iodide and bromide show that the diffracting centres are arranged on a lattice whose element is the face-centred cube. Sodium chloride is an intermediate case. From this and other features of the diagrams, it is concluded that in all these crystals the atoms of metal and halide are arranged in a simple cubic lattice, rows parallel to the axes containing alternate atoms of either kind. In sylvine the equal weights of the atoms render them equally efficient as centres; in KBr and KI the heavy halogen atoms alone act, and so the pattern is characteristic of the face-centred cube lattice. The diagrams of other crystals are discussed in reference to these conclusions.

By means of the X-ray spectrometer, described in a previous paper, the dimensions of these lattices can be accurately compared; and the relative magnitudes of the different orders of spectra reflected from any face, and from different crystals, yield information which confirms the above conclusions. It also appears that the weight associated with each point of the lattice is proportional to the molecular weight of the substance. These conclusions yield the necessary information for the accurate calculation of the wave-length of the X-ray.

"*Resonance of the Tissues as a Factor in the Transmission of the Pulse and in Blood Pressure.* By Leonard Hill, F.R.S., J. M. McQueen, and W. W. Ingram.

"*Experiments on the Flow of Viscous Fluids through Orifices.*" By G. F. Davidson.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 21).

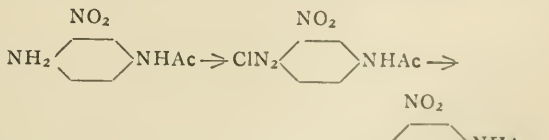
206. "*Influence of Substitution on the Reactivity of* p-*phenylenediamine.*" By Gilbert T. Morgan and Joseph Allen Pickard.

This investigation, which is a contribution to the study of the inhibition of chemical change, was initiated with the object of ascertaining the part played by substituents in modifying the reactivity of *p*-phenylenediamine and its homologues. The following preliminary experiments were carried out on two derivatives of this diamine containing negative substituents.

I. *The Reactivity of Nitro-*p-*phenylenediamine.*

1. *Acetylation.*—One acetyl group only was introduced into the molecule of this nitrodiamine by suspending the base in water, adding excess of acetic anhydride, and subsequently heating to boiling. The product, which crystallised from water in light red, felted needles, melting at 189°, was identical with the monoacetyl derivative previously obtained by half hydrolysing nitrodiacetyl-*p*-phenylenediamine with ammonia, dilute aqueous alkalis, or preferably with baryta water (*Ber.*, 1884, xvii., 148; 1886, xix., 339; 1897, xxx., 980; 1903, xxxvi., 415).

As the constitution of this compound has been assumed without proof, it was dissolved in cold alcohol and treated successively with hydrogen chloride and nitrous fumes, the diazonium chloride being precipitated with dry ether. This salt was suspended in absolute alcohol, the mixture warmed with copper powder, and the solution neutralised with calcium carbonate, filtered, and evaporated nearly to dryness. *m*-Nitroacetanilide (m. p. 150°) separated, and was further identified by hydrolysis to *m*-nitroaniline (m. p. 112°). These reactions fix the constitution of the acetyl derivative as 2-*nitro*-4-*acetyl*-p-*phenylenediamine*, —



Acetylation with acetic anhydride in the presence of water leads to diacetyl derivatives with *p*-phenylene-

diamine and its homologue, 2 : 5 tolylenediamine; it is also practicable with *m*- and *p*-nitroanilines, but not with *o*-nitroaniline.

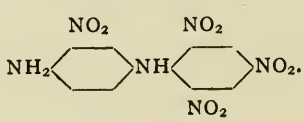
2. *Picrylation.*—Only one picryl group is introduced by boiling nitro-*p*-phenylenediamine for twelve hours with excess of picryl chloride (3 mols.) in dry toluene over anhydrous sodium acetate.

*Nitro-4-picryl-*p*-phenylenediamine*, which separated in dark red crystals melting at 255°, dissolved in aqueous or alcoholic sodium hydroxide, and was only sparingly soluble in alcohol, glacial acetic acid, or concentrated hydrochloric acid :—

0·2028 gave 39·1 cc. N_2 at 15° and 766 mm. N = 22·77.
$C_{12}H_8O_8N_6$ requires N = 23·10 per cent.

Comparative experiments with *o*-nitroaniline and 2 : 4-dinitroaniline showed that these bases are not picrylated under the foregoing conditions, and it is accordingly highly probable that in nitro-*p*-phenylenediamine picrylation occurs in the amino-group remote from the nitro-radicle. Direct evidence was obtained by dissolving the picryl derivative in concentrated sulphuric acid and adding successively to the bright yellow solution nitrosyl sulphate and alcohol, the temperature being kept below 5°. The solution of diazonium sulphate thus produced gave a deep red azo-β-naphthol derivative, dissolving in concentrated sulphuric acid to a bluish green solution.

When boiled with copper powder, the alcoholic solution of the diazonium salt evolved nitrogen, and yielded picryl-*m*-nitroaniline (m. p. 207°), thus indicating the following constitution for the picrylated diamine :—



3. *Diazotisation.*—Although nitro-*p*-phenylenediamine diazotises most readily to the monodiazonium salt (Bülow, *Ber.*, 1896, xxix., 2285) in 50 per cent sulphuric acid, the second amino-group is attacked, with the production of the bisdiazonium sulphate. These reactions have been turned to account in the preparation of 4-nitro-*m*-toluidine. The homologous base, 4-nitro-2 : 5 tolylenediamine, behaved in a similar manner, diazotising chiefly to 4-nitro-5-aminotoluene-2-diazonium chloride with a smaller proportion of 4-nitrotoluene-2 : 5-bisdiazonium chloride.

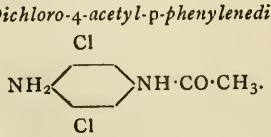
II. *The Reactivity of* 2 : 6-*Dichloro-*p*-phenylenediamine.*

1. *Acetylation.*—When boiled with acetyl chloride, 2 : 6 dichloro-*p*-phenylenediamine yielded 2 : 6-*dichlorodiacetyl-*p*-phenylenediamine*, which crystallised from alcohol or hot water in colourless needles, melting at 253—254° :—

0·1722 gave 15·4 cc. N_2 at 12° and 757 mm. N = 10·5.
$C_{10}H_{10}O_2N_2Cl_2$ requires N = 10·73 per cent.

When boiled for fifteen minutes with N-sodium hydroxide solution (30 parts), the diacetyl derivative yielded a monoacetyl compound, crystallising from alcohol in lustrous, colourless plates, melting at 218°, and dissolving in dilute hydrochloric acid, the soluble hydrochloride being readily diazotised.

2 : 6-*Dichloro-4-acetyl-*p*-phenylenediamine*,



This isomeric monoacetyl derivative was produced by shaking 2 : 6-dichloro-*p*-phenylenediamine with excess of acetic anhydride and water. It crystallised from alcohol or water in colourless needles, melting at 200° :—

0·1553 gave 17·3 cc. N_2 at 18° and 759 mm. N = 12·85.
$C_8H_8ON_2Cl_2$ requires N = 12·70 per cent.

The constitution of this compound was determined by adding nitrosyl sulphate to its slightly warm solution in absolute alcohol. The diazonium sulphate, which separated in colourless, feathery needles, was suspended in alcohol and treated with copper powder, when a brisk evolution of nitrogen occurred. 3 : 5-Dichloroacetanilide (m. p. 187°) separated in colourless crystals on diluting the filtered solution with water, and this product, when hydrolysed with concentrated hydrochloric acid, yielded 3 : 5-dichloroaniline (m. p. 51°).

2. *Picrylation.*—Only one amino-group is picrylated on boiling 2 : 6 dichloro-*p*-phenylenediamine with picryl chloride in toluene solution over anhydrous sodium acetate.

2 : 6-*Dichloropicryl-*p*-phenylenediamine*,

$$NH_2 \cdot C_6H_2Cl_2 \cdot NH \cdot C_6H_2(NO_2)_3,$$

separated from glacial acetic acid in lustrous, dark red crystals, sintering at 220° and melting at 227—228° :—

0·1516 gave 0·1119 AgCl. Cl = 18·25.
$C_{12}H_7O_7N_5Cl_2$ requires Cl = 18·27 per cent.

The compound was soluble in aqueous or alcoholic alkali hydroxides, but dissolved only very sparingly in hydrochloric acid.

3. *Diazotisation.*—2 : 6-Dichloro-*p*-phenylenediamine did not diazotise smoothly in aqueous solutions of the mineral acids, and although the reaction proceeded more readily in alcoholic or glacial acetic acid solution, even then only one amino-group was diazotised with the formation of 2 : 6-dichloro-1-aminobenzene-4-diazonium chloride or sulphate. On treatment with absolute alcohol and copper powder, these diazonium salts yielded 2 : 6-dichloroaniline, thus showing that the amino-group diazotised is the one in the meta-position with respect to the chlorine atoms.

Summary.

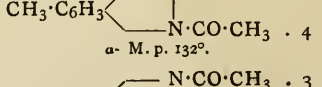
1. The introduction of a negative radicle into the aromatic nucleus of *p*-phenylenediamine hinders very considerably the acetylation of the amino-group contiguous to this substituent. The picrylation of this amino-group is completely inhibited.

2. The introduction of one nitro-group into the *p*-phenylenediamine or 2 : 5-tolylenediamine nucleus diminishes very considerably the diazotisability of the contiguous amino-group. The presence of two chlorine atoms in ortho-positions with respect to one amino-group of *p*-phenylenediamine inhibits completely the diazotisation of this group.

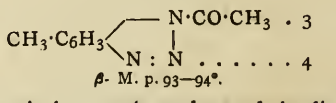
207. "*The Constitution of the Ortho-diazoimines.* Part III. *The α- and β Acyl-*3 : 4-*Tolylenediazoimides as Structural Isomerides.*" By Gilbert T. Morgan and Francis Mary Gore Micklethwait.

3 : 4-Tolylenediazoimine or its metallic derivatives yield on acetylation a mixture of two acetyl derivatives, which have hitherto been regarded as "physical isomerides" (Zincke and Lawson, *Ann.*, 1887, ccxl., 119).

The authors have shown that these compounds are structural isomerides having the constitutional formulæ :—



α- M. p. 132°.

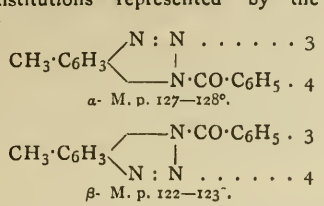


β- M. p. 93—94°.

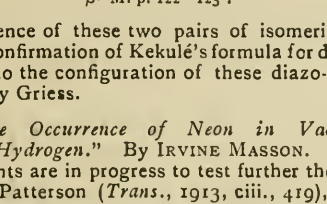
arising respectively as sole products of the diazotisation of 4-acetyl-3 : 4 tolylenediamine and 3-*acetyl*-3 : 4-*tolylenediamine*.

The chemical nature of the foregoing case of isomerism was confirmed by obtaining from 4-benzoyl-3 : 4-tolylenediamine and 3-*benzoyl*-3 : 4-*tolylenediamine* respectively, the isomeric pair of *benzoyl*-3 : 4-*tolylenediazoimides*

having constitutions represented by the following formulæ :—



α- M. p. 127—128°.



β- M. p. 122—123°.

The existence of these two pairs of isomerides affords additional confirmation of Kekulé's formula for diazoimines as opposed to the configuration of these diazo-derivatives advocated by Griess.

208. "*The Occurrence of Neon in Vacuum-tubes Containing Hydrogen.*" By Irvine Masson.

Experiments are in progress to test further the results of Collie and Patterson (*Trans.*, 1913, ciii., 419), and have yielded independent evidence of the fact that neon appears after the passage of an electrical discharge through a vessel containing a gas previously free from neon.

When pure dry hydrogen was sparked in a discharge-tube bearing a perforated aluminium disk cathode and having a vacuous jacket surrounding it, it was found that after a time a neon ceased to be formed; on then admitting a mixture of oxygen and hydrogen and passing the discharge, the tube appeared to be rendered "active" once more, for thereafter neon was steadily produced when hydrogen was sparked.

In all these experiments, hydrogen accumulated in the initially vacuous jacket, and had apparently passed through from the discharge-tube. Quantities up to about one-third of a cc. could be so obtained. This gas was found to contain no other, except carbon monoxide in small and varying amounts.

209. "*A Simple and Efficient Method of Dehydrating Substances by Electrical Heating in a Vacuum.*" By William Ernest Stephen Turner and Crellyn Colgrave Bissett.

Methods of electrical heating within a vacuum desiccator have already been described by Skita (*Chem. Zeit.*, 1902, xxvi., 898) and by Scheermesser (*Ibid.*, 1903, xxvii., 175). The first-named author used two 16-candle-power lamps promoting a temperature of 70°; the second, a plate; and both methods are suitable more for the evaporation of liquids than for dehydration at higher temperatures.

The author's own method, which was in use some time before they were aware of previous arrangements, is not only much more efficient, but also far simpler. It consists in introducing into a vacuum desiccator a heating coil made of manganin wire, a length of 90 cm. of No. 20 wire gauge being very suitable, so as to give a coil of about 4 cm. internal diameter. A cover for the coil is made by wrapping round it a strip of asbestos paper, previously moistened. Connexion is made with the coil by two leads of stout copper wire, which pass through two pieces of narrow quill glass tubes inserted in the rubber stopper of the desiccator, the upper ends of the glass tubes being then closed by sealing wax.

Using a small platinum dish, weighing 12 grms., 3·5 grms. of powdered silica were maintained in the exhausted desiccator at a temperature of 36° with a current of 2 amperes, 92° with 4 amperes, and 154° with 5·8. Still higher temperatures may be reached if desired. The drying agent used in the desiccator is phosphoric oxide.

The value of the method will be realised by the two following cases, in which dehydration by previous methods appears to have been both difficult and not entirely successful.

Lithium iodide at the ordinary temperature occurs as the trihydrate, although the commercial samples are usually partly dehydrated. In Abegg's "Handbuch der anorganischen Chemie," vol. II., p. 130, it is stated that the anhydrous form may be produced by heating above 300°, but that the substance so obtained is not pure, since at this temperature it attacks glass and porcelain. From the authors' tests, a sample of the salt of composition corresponding precisely with the monohydrate did not lose moisture by standing over phosphoric oxide in an exhausted desiccator for three weeks. By the new process, pure anhydrous lithium iodide (Found, I = 94 9. Calc., I = 94·8 per cent.) was obtained after raising the temperature to about 100° for several hours. The iodide so obtained is quite white.

Rhamnose is another substance the dehydration of which up to now has proved very difficult. It occurs ordinarily combined with one molecule of water, and its dehydration not only requires prolonged heating on a water-bath, but the process is also accompanied by at least a partial conversion into the β-form. Purdie and Young (*Trans.*, 1906, lxxxix., 1194) state that dehydration is incomplete after prolonged heating at 70—90° under diminished pressure and in presence of phosphoric oxide, and is accompanied in this case also by partial conversion into the β-form. The authors have been successful in completely dehydrating rhamnose during the course of a week by raising the temperature within the exhausted desiccator very slowly to about 90°. Moreover, polarimetric observations (made by Mr. C. R. Young) point to the absence of the β-form from the dehydrated sugar.

210. "*The Vapour Density of Ammonium Nitrate, Benzoate, and Acetate.*" By Prafulla Chandra Ray and Sarat Chandra Jana.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, vol. xxix., p. 28).

211. "*The Action of Nitric Oxide on a Neutral Solution of Potassium Permanganate.*" By Barum Chandra Dutt, Bamacharan Chatterji, and Haridas Banerji.

When nitric oxide is passed through a solution of potassium permanganate in an atmosphere of hydrogen, the reaction which takes place is represented by the equation $KMnO_4 + NO = KNO_3 + MnO_2$.

There is no intermediate formation of nitrous acid.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. IV. Oilstone to Soda Nitre. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The fourth volume of the new edition of this valuable dictionary contains some very lengthy and highly important articles on subjects of great technical interest; for example, rubber, petroleum, paints, &c., while the more purely scientific side of the subject is given adequate consideration. The names of the contributors include those of the best known experts in every branch of applied chemistry, and the fourth volume is in every respect fully up to the level of its predecessors.

Manual of Qualitative Analysis. By Wilbur F. Hoyt, A.B., A.M. New York: The Macmillan Co. 1913.

The methods generally employed in the qualitative analysis of inorganic compounds are briefly described in this small book, which is characterised by great conciseness. Wet tests for the commoner metals and acid radicles are given in the most condensed form possible, and all difficult equations are group together, while the simpler are given in the descriptions of the tests. Some notes on valence and the

writing of equations are added, and a few simple tests for the examination of drinking water are included. Dry tests are described in the later parts of the book, and it is recommended that their application should be deferred until the student is doing his second year's work in the laboratory, a plan which is not usually regarded as advisable.

Liquid Air, Oxygen, Nitrogen. By GEORGES CLAUDE. Translated by HENRY E. P. COTTRELL. London: J. and A. Churchill. 1913.

THIS translation will be much appreciated in England, where for some time the need has been felt of an authoritative and comprehensive standard work on the liquefaction of gases and the use of liquid air. The author has done some valuable pioneering work on the subject, and his experiments have done much to further the liquid air industry. The book is written in a very interesting and graphic style, and gives a detailed description of the early experiments which led up to the liquefaction of the so-called permanent gases and of the chief processes for the commercial preparation of liquid air. The properties of liquid air are fully discussed, many striking experiments which can be performed with it being outlined, while some remarkable illustrations are included. The separation of the air into its elements and the cheap manufacture of oxygen on a large scale are treated in Part IV., and some installations of different systems in Germany and France are described. Theoretical considerations are by no means neglected, and the book provides an admirable survey of the theory and practice of the liquefaction of air.

Chloride of Lime in Sanitation. By ALBERT H. HOOKER. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THE research department of the Hooker Electrochemical Company, on the advice of Dr. L. H. Baekeland, President of the American Institute of Chemical Engineers, recently undertook to collect all available data relating to the use of chloride of lime in sanitation, and the amount of material brought together was so large and appeared of such great value that it was decided to publish it in book form. Sanitary officials in this country should be grateful for this decision, more particularly as the book contains short abstracts of a large number of articles on sanitation which have appeared in various journals and which are referred to in the text. These abstracts are arranged under convenient headings and the book is well indexed. For its treatment of the subject of the campaign against the house fly alone it is an important contribution to the literature of sanitation which should be in the hands of all who are in charge of work connected with the public health.

Jahrbuch der Organischen Chemie. ("Year Book of Organic Chemistry.") By Professor Dr. SCHMIDT. Sixth year. Leipzig: Johannes Wörner. 1913.

A DETAILED survey of the progress in organic chemistry made during the year 1912 is given in this book. In the first and general section the important work which has been done on the stereo-chemistry of carbon and nitrogen is summarised, and Wörner's work on the isomerism of Co, Rh, Cr, and Fe compounds is discussed. The study of the physical properties or organic compounds has recently made considerable advances, and the work of K. v. Auwers and others appears to be leading to important developments, as is duly pointed out. In the special part the many new syntheses which have been effected are described as well as experiments which have thrown light upon the constitution of important compounds. The chemistry of chlorophyll is discussed at some length and also the preparation of synthetic rubber. The year book contains a list of works on organic chemistry which were published in the German language during the year 1912, and also a few short obituary notices.

Directory of Paper Makers of the United Kingdom for 1913. London: Marchant, Singer, and Co.

THE 1913 edition of the Paper Makers' Directory has been thoroughly revised and numerous additions have been made to the list of trade designations. A complete catalogue of actual watermarks is given, and another of trade names which are not watermarks. In addition the directory contains some short notes on paper trade customs.

CORRESPONDENCE.

CHROMATE AND BICHROMATE OF POTASSIUM OR SODIUM.

To the Editor of the Chemical News.

SIR,—I am directed by the Secretary of State to transmit to you herewith a copy of a draft of Regulations which he proposes to make under Section 79 of the Factory and Workshop Act, 1901, for the manufacture of chromate and bichromate of potassium or sodium.—I am, &c.

H. W. ROBINSON,
Deputy Chief Inspector of Factories.

Home Office, July 9, 1913.

Definitions.

(Terms to which defined meanings are given are printed throughout the Regulations in *italics*).

In these Regulations:—

"*Chrome process*" means manipulation, movement, or other treatment of chromate or bichromate of potassium or sodium.

"*Surgeon*" means the Certifying Factory Surgeon of the district or a duly qualified medical practitioner appointed by written certificate of the Chief Inspector of Factories, which appointment shall be subject to such conditions as may be specified in that certificate.

"*Suspension*" means suspension from employment in any *chrome process* by written certificate in the Health Register, signed by the *Surgeon*, who shall have power of *suspension* as regards all persons employed in any *chrome process*.

"*Efficient exhaust draught*" means localised ventilation effected by heat or mechanical means, for the removal of steam or dust so as to prevent them from escaping into the air of any place in which work is carried on.

Duties.

It shall be the duty of the occupier to observe Part I. of these Regulations.

It shall be the duty of every person employed to observe Part II. of these Regulations.

Part I.—Duties of Occupiers.

1. With regard to every uncovered fixed vessel, whether pot, pan, vat or other structure, containing any corrosive liquid.

(*a*) Each such vessel shall, unless its edge is at least 3 feet above the adjoining ground or platform, be securely fenced;

(*b*) For the purposes of paragraph (*a*) of this Regulation no fencing shall be deemed to be secure unless it extends to a height of at least 3 feet above the adjoining ground or platform: provided however that Paragraph (*b*) of this Regulation shall not apply:—

(i.) to any vessel constructed before 1st January, 1899; or

(ii.) where a height of 3 feet is impracticable by reason of the nature of the work to be carried on;

(*c*) No plank or gangway shall be placed across any such vessel unless such plank or gangway is—
(i.) at least 18 inches wide; and
(ii.) securely fenced on both sides; either by upper and lower rails, to a height of 3 feet, or by other equally efficient means;
(*d*) Where such vessels adjoin, and the space between them either—
(i.) affords foothold, and is not fenced as in paragraph (*c*) (ii.) of this Regulation, or
(ii.) is less than 18 inches in width, clear of any brick or other work surrounding them,
a secure barrier shall be so placed as to prevent passage between them.

2. All dangerous places near to which persons are employed, or near to which they have to pass, shall be efficiently lighted by day and night.

3. Grinding, unless done with slow moving edge runners, and sieving the raw materials, evaporating, and packing shall not be carried on except either—
(*a*) with an *efficient exhaust draught;* or
(*b*) in such manner as will prevent escape of dust or fume into the air of any place at which work is carried on.

4. No person under eighteen years of age and no female shall be employed in any *chrome process*.

5.—(*a*) Every person employed in a *chrome process* shall be examined by the *Surgeon* once in every calendar month on a date, or dates, of which due notice shall be given. The *Surgeon* shall undertake any necessary medical treatment of lesions contracted in consequence of such employment.
(*b*) A Health Register containing the names of all persons employed in any *chrome process* shall be kept in a form approved by the the Chief Inspector of Factories.
(*c*) No person after *suspension* shall be employed in any *chrome process* without written sanction from the *Surgeon*, entered in the Health Register.

6. Requisites (approved by the *Surgeon*) for treating slight wounds and ulcers shall be kept at hand and be placed in charge of a responsible person.

7. There shall be provided—
(*a*) sufficient and suitable overall suits for the use of all persons engaged in grinding the raw materials, which overall suits shall be washed, cleaned, or renewed at least once every week; and
(*b*) sufficient and suitable protective coverings for the use of all persons engaged in the crystal department and in packing;

8. There shall be provided suitable respirators for the use of all persons employed in packing bichromate of potassium or sodium; which respirators shall be washed or renewed at least once every day.

9. There shall be provided and maintained for the use of all persons employed in any *chrome proeess*—
(*a*) a suitable meal room;
(*b*) a suitable place or places for clothing put off during working hours; and
(*c*) a suitable place or places for the storage of overall suits provided in pursuance of Regulation 7 (*a*); which place or places shall be separate from that required by paragraph (*a*) of this Regulation.

10. There shall be provided and maintained in a cleanly state and in good repair for the use of all persons employed in any *chrome process*—
(*a*) a lavatory, under cover, with a sufficient supply of clean towels, renewed daily, and of soap and nail brushes, and with either—
(i.) a trough with a smooth impervious surface fitted with a waste-pipe, without plug, and of sufficient length as to allow of at least two feet for every five such persons employed at any one time, and having a constant supply of warm water from taps or jets above the trough at intervals of not more than two feet; or
(ii.) at least one lavatory basin for every five such persons employed at any one time, fitted with a waste-pipe and plug, and having either a constant supply of hot and cold water or warm water laid on, or (if a constant supply of heated water be not reasonably practicable) a constant supply of cold water laid on, and a supply of hot water always at hand when required for use by such persons;
and for the use of all persons employed in the crystal department or in packing—
(*b*) sufficient and suitable bath accommodation with hot and cold water laid on and a sufficient supply of soap and towels.

11. A Bath Register shall be kept containing a list of all persons employed in the crystal department and packing, and an entry of the date when each person takes a bath.

Part II.—Duties of Persons Employed.

12. Every person employed in a *chrome process* shall present himself at the appointed time for examination by the *Surgeon*, in pursuance of Regulation 5 (*a*).

13. No person employed shall, after *suspension*, work in any *chrome process* without written sanction from the *Surgeon*, entered in the Health Register.

14. Every person employed in any *chrome process* shall deposit in the place or places provided in pursuance of Regulation 9 (*b*) all clothing put off during working hours.

15. Every person for whose use an overall suit is provided in pursuance of Regulation 7 (*a*) shall wear the overall suit when employed in grinding the raw materials, and, on leaving the premises, deposit it in the place provided under Regulation 9 (*c*).

16. Every person for whose use a respirator is provided in pursuance of Regulation 8 shall wear the respirator while employed in packing.

17. Every person employed in grinding the raw materials, or in the crystal department, or in packing, shall, before leaving the premises, thoroughly wash the face and hands.

18. Every person employed in the crystal department or in packing shall take a bath at the factory at least once a week; and, having done so, he shall at once sign his name in the Bath Register with the date; provided that
This Regulation shall not apply in the case of a workman who is unwell.

19. No person shall take a meal in the crystal department.

20. No person employed shall interfere in any way, without the concurrence of the occupier or manager, with the means provided for the carrying out of these Regulations.

DESTRUCTION OF ROOTS OF TREES.

To the Editor of the Chemical News.

Sir,—I have acquired about 20 acres of land lately covered with timber (fir). The timber has been sawn off as close to the ground as possible, and the job of getting the roots out is much more laborious and slow than I thought it would be. Could you tell me if there is any chemical, acid, or oil that would consume or rot them quickly in the ground? In the ordinary course of nature I suppose they would rot away in about ten years, but I would like it broken up and under crop much earlier than that.—I am, &c.,

William Malloy.

Reaction of Nitroprussiate with Acetone.—Livio Cambi.—It has long been known that nitroprussiates give a colour reaction with acetone in presence of alkali, but the mechanism of the reaction was unknown. The author has now shown that the coloration is due to the formation of isonitrosoketones. All ketones and aldehydes with the group —CO—CH_n— give the reaction; acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$, gives it very strongly.—*Atti della Reale Accademia dei Lincei*, xxii., No. 6.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 18, May 5, 1913.

Preparation of Barium.—Camille Matignon. — To prepare metallic barium a mixture is made of 3 parts of BaO to 1 atom of silicon, and it is placed in a steel tube, closed at one end, and heated to 1200° in a porcelain tube in which a vacuum is maintained. The metal distils and condenses on the cooler parts of the steel tube. Without taking any special precautions the author thus obtained a specimen containing 98·5 per cent of barium. Pure amorphous silicon can be used, or a rich ferro-silicon.

Action of Reducing Agents on Chloraloses.—M. Hanriot and A. Kling.—Aluminium amalgam in acid or neutral medium removes 1 atom of chlorine from the molecule of a chloralose. Sodium amalgam in an acid medium gives the same reaction, but it also with difficulty removes a second chlorine atom, while in an alkaline medium the second reaction predominates. Sodium dissolved in liquid ammonia removes 3 atoms of chlorine from chloraloses, the product of the reaction being complex.

Synthesis in the Indigoid Group.—A. Wahl and P. Bagard.—When oxindol condenses with isatin in concentrated sulphuric acid solution, sulphonation occurs and disulphonic isoindigotin acid is obtained. When isatin is replaced by its substituted derivatives disymmetrical substituted isoindigos are obtained. Chloride of isatin reacts with oxindol in a benzene medium to give indirubin, and the substituted isatin chlorides give substituted indirubins, which are violet-coloured dyes.

Preparation of Carbon Tetraiodide. — Marcel Lantenois.—Carbon tetraiodide can be prepared by heating lithium iodide with carbon tetrachloride in a sealed tube *in vacuo* for five days. The temperature must be kept at 90—92°, and after elimination of the excess of the tetrachloride the products of the reaction are taken up with water, and the iodide is separated off, washed, and dried. The yield is 33 per cent. The hydrated iodides of magnesium and zinc can be used for the same purpose, but owing to the readiness with which they are hydrolysed the iodide of carbon is rapidly transformed into iodoform by the hydriodic acid generated. When a very alkaline solution of potassium iodide is heated to 80—90°, a small proportion of acetone is added and then concentrated hypochlorite, tetraiodide of carbon is obtained containing only 10 per cent of iodoform. The tetraiodide can be extracted in a state of great purity by means of petroleum ether and benzine. It crystallises in ruby-coloured octahedra, possessing a very characteristic smell. Its density is 4·5 at 0°. Its best solvents are carbon disulphide, benzine, and acetone.

Vol. clvi., No. 20, May 19, 1913.

Monomethylcamphoroxime.—A. Haller and Edouard Bauer.—When methylcamphoroxime is prepared by means of chlorozincate of hydroxylamine two oximes are formed, one active and the other inactive. The raw oxime gives two phenylurethanes, the first of which is dextrotatory while the other is racemic. The dextro oxime gives rise to a dextro methylcampholenic nitrile, which on hydration yields inactive methylcampholenic amide, and on hydrolysis inactive methylcampholenic acid. Probably methylcampholenic nitrile is analogous to α-campholenic nitrile, and when it is hydrated and hydrolysed it undergoes molecular transposition, its derivatives being β-campholenic compounds.

Variations of Magnetic Rotatory Power in Changes of State.—J. Chaudier.—In the passage from the liquid to the solid state the magnetic rotatory power of active substances is unchanged if the liquid on congelation gives irse to an amorphous substance of vitreous appearance; on the other hand, it entirely disappears if the solid formed has a crystalline structure. The magnetic rotatory power of active substances in the gaseous state, calculated on the assumption that the phenomenon varies as the density, is higher than, or nearly equal to, the rotatory power as directly observed. Thus, while the ordinary rotatory power is preserved in the passage from the liquid to the gaseous state, the magnetic rotatory power generally diminishes, sometimes by one-half, and, moreover, there seems to be a relation between this variation and the magnetic rotatory dispersion of active substances.

System Manganese-silver.—G. Arrivaut.—The author has studied the system manganese-silver thermically, microscopically, and chemically, and has also determined the electromotive forces, using an electrode of silver depolarised with manganese dioxide and immersed in a 10 per cent solution of manganese sulphate. All these methods of investigation show that manganese and silver form a compound $MnAg_2$. This compound gives a continuous series of mixed crystals with silver, and the limit of its miscibility in the liquid state with manganese is at about 30 per cent of manganese.

Quantitative Study of the Absorption of Ultra-violet Rays by Alkaloids of the Atropine Group.—Marcel Gompel and Victor Henri. — The absorption spectrum of atropine shows three bands at $\lambda = 2645$, 2580, and 2505. The constitutional formula of apoatropine differs from that of atropine only in the existence of a double bond, and hence it would be expected that its absorption would be greater, which is found to be actually the case. The absorption spectrum of cocaïne is very different from those of the two preceding alkaloids. It possesses three bands at $\lambda = 2814$, 2722, and 2314, that at 2314 being very well marked.

Benzoyl Cyanhydrines of Ketones and the Amides and Acid Alcohols derived from them.—J. Aloy and Ch. Rabaut. — Good yields of the benzoyl cyanhydrines of ketones can be obtained if one molecule of KCN and one molecule of acetone are thoroughly shaken and one molecule of C_6H_5COCl is added drop by drop. The mixture has to be very thoroughly shaken, the operation taking two or three hours. The cyanhydrines are generally well crystallised stable compounds, which are readily transformed into the corresponding benzoyl amides and into tertiary acid alcohols containing no benzoyl group.

Characterisation of Chlorinated Ketones.—E. E. Blaise.—In order to identify the chlorinated ketones it is most convenient to prepare the normal semicarbazones, which possess conveniently low fusion points. Nearly all chlorinated ketones are rapidly converted into semicarbazones by the action of 1 to 1·5 mol. of hydrochloride of semicarbazide dissolved in water.

MISCELLANEOUS.

Action of Alkaline Sulphites on Ethylenic Acids. —J. Bougault and M. Mouchel-la Fosse.—Many acyclic and cyclic ethylenic acids combine with sodium bisulphite to give the sodium salts of sulphonic acids by fixation of the bisulphite at the double bond. The fixation occurs more easily and rapidly the more electronegative groups the ethylenic acid contains. The sulphonic acids obtained are very soluble in water, even when they are derived from insoluble acids. By means of this reaction it is possible to determine approximately the amount of ethylenic acid present in a mixture with saturated acids, and to separate the saturated acids in a state of purity. —*Journal de Pharmacie et de Chimie*, vol. vii., No. 10.

ERRATUM.—P. 16, col. 1, line 22, *read* "*Zeit. Anorg. Chem.*, 1913 Bd. 82, p. 249."

THE CHEMICAL NEWS.

Vol. CVIII., No. 2800.

THE WALDEN REACTION.

By CECIL L. HORTON.

This reaction seems to affect only the α- and β-amino-halogen and hydroxy acids. These acids, however, may be either secondary or tertiary. The changes may be

$$NH \rightleftharpoons OH \rightleftharpoons Cl$$

represented by $\longrightarrow$.
$\longleftarrow$

The reagents employed are NOBr, NOCl, NH_3, PCl_5, $SOCl_2$, Ag_2O, KOH, HNO_2, KNO_2 and HCl, MeOH, and H_2O.

In only one case does the reagent exhibit a constant behaviour, that is in the case of PCl_5. In all other cases the sign of the active product is sometimes the same as and sometimes the opposite to that of the parent body. There seems to be no experimental evidence as to whether thionyl chloride is constant in its behaviour or whether it resembles the other reagents.

Disregarding the exception named above, it would seem that the direction of the reaction is dependent on the number of free carboxyls. For an even number of free carboxyls the influence on the sign of the active body is the reverse of that if the number of free carboxyls be odd.

Omitting the constant reagent, the following table shows the effect on acids with one free carboxyl:—

Reagent.	Direction of reaction.
$SOCl_2$	*d*——*d*
Ag_2O	*d*——*l*
KOH, NaOH, $NaOCH_3$	*d*——*d*
NOBr, NOCl	*d*——*l*
H_2O	*d*——*l*
NH_3	*d*——*d*
HNO_2	*d*——*l*

Thus NOBr on *d*-alanine ester (no free carboxyl) gives rise to *d*-α-bromopropionic ester. On the other hand, the same reagent on *d*-alanine itself (one free carboxyl) gives rise to *l*-α-bromopropionic acid.

From the twenty-six examples given above there seems to be only one exception, that of *d*-a-bromoisovaleric acid, which under the influence of ammonia gives rise to *l*-valine when the *d*-isomer would be expected. It is thus possible to predict the sign of any product under the influence of any definite reagent by studying the number of free carboxyl groups present.

The behaviour of the dialkyl esters of dibasic acids and of the mono- di-, and tri-alkyl esters of the tri-basic acids, &c., would be of interest.

Reagent.	Reaction.		No. of free carboxyls.
Ag_2O	*l*-α-Bromopionic acid	*d*-Lactic acid	1
	l-Phenylchloracetic acid	*d*-Mandelic acid	1
	l-Chlorsuccinic acid	*l*-Malic acid	2
	l a-chlor-α-phenyl propionic acid	*d*-α-Hydroxy acid	1
KOH	*d*-Chlorpropionic	*d*-Lactic acid	1
NaOH	*d*-Clorsuccinic	*l*-Malic acid	2
	d-Phenylchloracetic acid (In general, the reverse of silver oxide).	*d*-Mandelic acid	1
MeONa	*d*-Phenylchloracetic acid	*d*-Methoxy acid	1
PCl_5	Always constant.	Change *l*-d	
$SOCl_2$	*l*-α-Hydroxy - α- phenyl-propionic acid	*l*-Chlor acid	1
	d-β-Hydroxy-β-phenyl-propionic acid	*d*-β-Chlor acid	1
H_2O	*l*-β-Chlorbutyric acid	*d*-β-Hydroxy acid	1
	l - β - Chlorphenylpropionic acid	*d*-β-Hydroxy acid	1
HNO_2	*d*-β-Aminobutyric acid	*l* - β - Hydroxy-butyric acid	1
	l-Asparine	*l*-Malic acid	2
	l-Aspartic acid	*l*-Malic acid	2
	l-Asparine probably passes through *l*-aspartic acid		
NOCl	*l*-Asparine	*l*- Chlorsuccinic acid	2
	l-Aspartic acid	*l*- Chlorsuccinic acid	2
NOBr	*d*-Alanine ester	*d* - α - bromopropionic ester	0
	d-Alanine	*l*-α - Bromopropionic acid	1
	l Aspartic ester (mono)	*d*-Bromosuccinic ester (mono)	1
	l Aspartic acid	*l*-Bromosuccinic acid	2
	l-Valine	*d*-α - Bromoiso valeric acid	1
NH_3	*l*-α-Bromopropionic acid	*l*-Alanine	1
	d-α-Bromoisovaleric acid	*l*-Valine	1(*a*)
	d - α - Bromoisovaleryl glycerine	*d* - Valine (on hydrolysis)	1

(*a*) The exception named above.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER.*

New Evidence for the Solvate Theory of Solution.

By J. SAM GUY, E. J. SHAEFFER, and HARRY C. JONES.

(Concluded from p. 30).

When salts which are strongly hydrated in aqueous solutions are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected, since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in Table V. bring out this fact.

The depth of layer of the different solutions for which the results are recorded in Table V. was the difference between 21 and 1 mm., *i.e.*, 20 mm. The results are, therefore, comparable with those recorded in Table III., the difference being a difference in the concentrations of the solutions used. It will be seen from a glance at the table that the difference between the transmission of the solution and that of water at the same depth as the water in the solution is very much less for the more dilute than for the more concentrated solutions. As has already been pointed out, this is exactly what would be expected in terms of the solvate theory applied to the phenomenon in in question.

Considerable work was done in *comparing directly* the transmission of a solution and that of water having the same depth as the water in the solution in question. The deflection of the radiomicrometer as given by the solution is in the column marked "I sol." and the deflection as given by water having the same depth as water in the solution is given in the column marked "I_0 H_2O."

* From the *American Chemical Journal*, xlix., No. 4.

Table V.

λ.	2·69/N $CaCl_2$. I/I_0.	H_2O.	2·48/N $MgCl_2$. I/I_0.	H_2O.	0·508/N $Al_2(SO_4)_3$. I/I_0.	H_2O.
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96
818	93	97	91	93	95	96
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1007	38	40	41	42	40	40
1013	39	42	40	44	40	40
1019	40	43	40	44	41	41
1025	43	45	44	41	43	43
1032	45	47	47	44	45	46
1037	48	50	50	46	47	48
1042	51	52	52	48	49	49
1046	56	56	56	54	53	54
1059	61	59	58	55	60	59
1065	65	64	64	62	59	62
1072	69	67	67	64	63	65
1078	70	69	69	67	65	69
1085	72	72	72	68	68	72
1100	73	73	73	71	69	73
1113	72	74	74	72	68	74
1138	72	74	74	70	67	72
1148	66	69	69	67	64	67
1158	67	62	62	60	58	62
1165	57	58	58	58	54	54
1172	52	51	53	52	47	46
1179	46	39	42	42	39	35
1186	30	27	31	27	28	25
1193	20	19	21	20	20	16
1200	13	14	15	15	14	12
1206	12	11	12	13	12	10
1213	11	11	12	12	11	10
1220	11	10	11	11	11	10
1227	10	9	10	10	10	9

Table VI.

λ.	I sol./$Al_2(SO_4)_3$.	I_0/H_2O.	I sol./KCl.	I_0/H_2O.
710	50	51	53	53
724	58	58	56	56
741	62	63	67	68
760	72	72	77	77
776	75	76	88	90
798	83	83	98	99
818	82	82	108	109
836	93	94	116	116
855	97	97	124	124
878	105	105	129	130
900	105	105	140	138
922	112	112	140	140
947	113	113	142	142
958	109	106	136	136
964	107	100	129	125
969	104	93	118	116
974	98	83	108	106
979	93	73	92	92
982	82	66	83	83
985	80	64	78	80
991	78	62	78	80
1007	78	65	78	81
1013	74	65	81	85
1019	77	68	84	88
1025	80	75	96	96
1032	84	77	100	101
1037	91	84	112	108
1042	92	92	119	116
1046	99	99	125	120
1059	105	105	141	136
1065	109	112	150	145
1072	114	119	169	153
1078	118	125	164	158
1085	122	132	168	164
1100	128	140	176	172
1113	129	142	178	175
1138	127	142	174	170
1148	123	131	164	162
1158	112	118	161	159
1165	108	111	157	154
1172	99	94	132	126
1179	87	74	107	100
1186	68	49	73	66
1193	54	35	50	48
1200	42	26	24	36
1206	35	23	39	32
1213	30	21	25	30
1220	28	20	24	29
1227	26	19	24	28
1241	24	19	23	26
1255	23	18	25	27

The results obtained for aluminium sulphate having a concentration 1·02/N and for 4/N potassium chloride are given in Table VI. The depth of solution used was 20 mm. and the depth of water that of the water in the solutions in question.

In this work duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave-lengths studied. It was found that the readings for the different solutions of the same substance having the same concentration were, for a given wave-length, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

An examination of the tables of data for potassium chloride, ammonium chloride, and ammonium nitrate, that is, for those substances which, in aqueous solutions, combine with very little water, as was demonstrated by the freezing-point method, shows that for all wave-lengths studied the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work we supposed that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above-named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another, the dissolved substance having very little absorption over the region of wave-lengths studied in this investigation.

When we turn to the data in Tables III. and IV. very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride, and aluminium sulphate, that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory (Carnegie Institution of Washington, *Publication* No. 60). The solution in these

cases is often more transparent than the same amount of water that is contained in the solution.

That these relations may appear the more clearly, the results obtained for the above-named salts are plotted as curves in Figs. I. to VI. Fig. I. is the curve for calcium chloride having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method, *i.e.*, by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution, the difference in the depths of water in the two cases being just equal to the depth of water in 20 mm. of the solution in question. Fig. II. is the curve for calcium chloride with a depth of layer of 10 mm. (11—1). The data from which

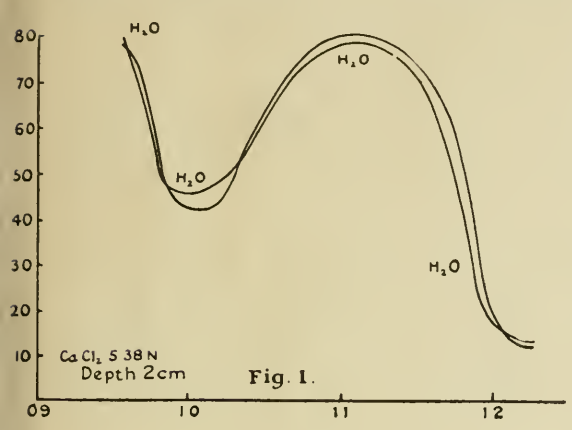


Fig. I.

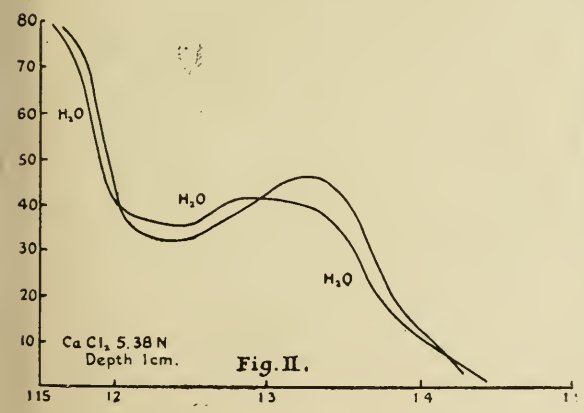


Fig. II.

the curve was plotted are contained in Table IV. The smaller depth of solution was used so that the water band between 1·2 μ and 1·3 μ would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water in this, as in all other cases, was obtained by the "differential" method.

Fig. III. is the curve for magnesium chloride having a depth of 21 − 1 = 20 mm. and the corresponding water curve. The data from which these curves are plotted are given in Table III.

Fig. IV. is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from Table IV.

Fig. V. is the curve for aluminium sulphate having a depth of 20 − 1 = 20 mm. and the corresponding absorption curve for water.

Fig. VI. is the curve for aluminium sulphate having a depth of 11 − 1 = 10 mm. and the corresponding water curve.

Fig. I. shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5·3 normal and a depth of 20 mm. The corresponding water curve is marked throughout by the symbol "H_2O." The solution is the more transparent from 0·9 μ to nearly 1 μ. The water then becomes the more transparent over a short region of wave-lengths. From 1·05 μ to 1·2 μ the solution is the more transparent. In this region the solution becomes as much as 25 per cent more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solutions which are vertically above

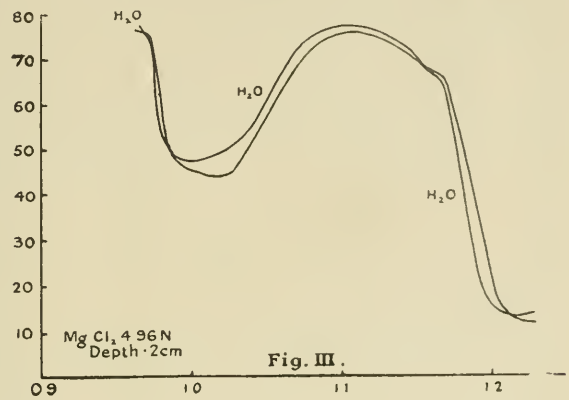


Fig. III.

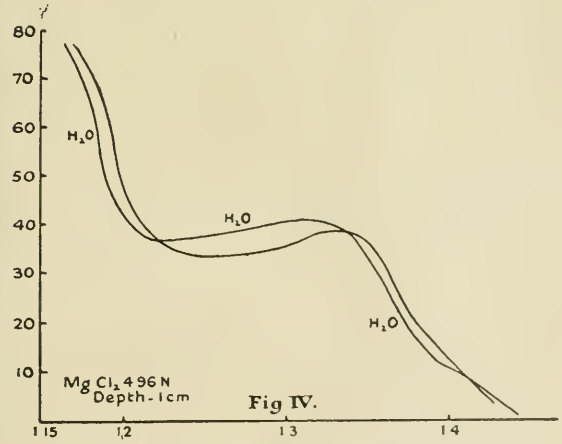


Fig IV.

the points on the water curve. The water becomes appreciably more transparent only at and near the bottom of the "water band" having a wave-length of approximately 1 μ. This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of non-hydrating and strongly hydrating salts as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in Fig. II. are for a smaller depth of the same solution of calcium chloride. This figure brings out

the same general relations as was shown in Fig. I. The water curve in the region 1·25 μ is above that of the solution, showing that water in this region for the more shallow depth of solution is more transparent than the solution. The additional feature brought out by this figure is the water band in the region 1·4 to 1·5 μ. After the first-named water band is passed the solution becomes more transparent than the water, and remains so until the wave-length 1·42 μ is reached. Here both the solution and the water are practically opaque, as is shown by both the curves approaching the abscissæ.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1·0 μ to 1·1 μ. In the case of magnesium chloride the water

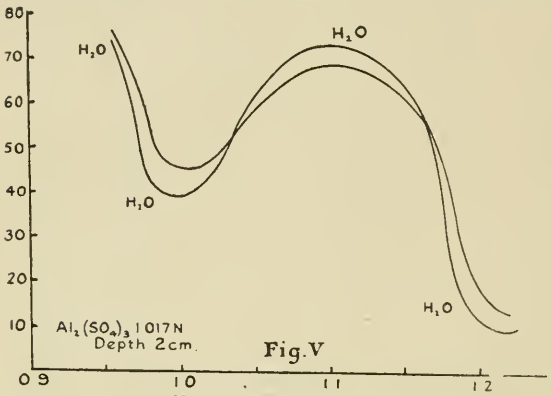


Fig.V

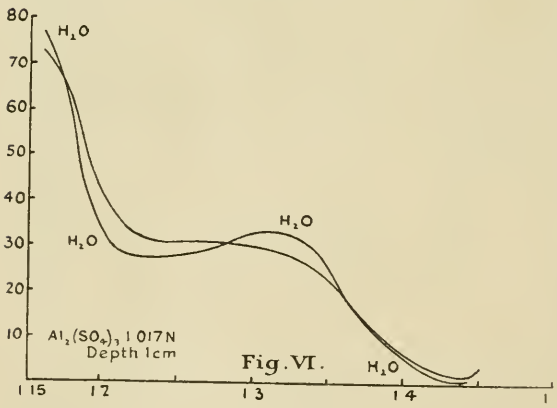


Fig.VI.

remains the more transparent over this region of wave-lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solu tion throughout the region is, however, not very great. From 1·1 μ towards the longer wave-lengths, as we come down the descending arm of the curve towards the second water band, the water in the case of the magnesium chloride, as in the case of calcium chloride, becomes much more transparent than the solution, the differences here being of the same order of magnitude as those with calcium chloride.

Fig. IV. gives the results for magnesium chloride with a depth of layer of 1 cm. The same relations hold in Fig. IV. as in Fig. III., for the relative transparency of the water and of the solution. The water becomes the more transparent from 1·22 μ to 1·34 μ. For the longer wave-lengths the solution becomes more transparent until the region 1·41 μ is passed. For wave-lengths longer than 1·41 μ the transmission of both solution and water is practically zero, that is, they both become opaque to the longer wave-lengths.

The results in Fig. V. bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave-length 1 μ the solution is more transparent than the corresponding water. Beyond the wave-length 1·04 μ the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave-length 1·6 μ the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

If we turn to Fig. VI. the relations are as follows:—In the region of 1·2 μ the water is more opaque. From 1·209 μ to 1·306 μ the water becomes the more transparent. From 1·306 μ to the longest wave-length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained bearing on this problem leads us to conclude that the greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved substance on the solvent water. The question remains, what is this action ?

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson (Carnegie Institution of Washington, Publication No. 110), and a large number of examples of this effect have since been found by Jones and Strong (*Ibid.*, Nos. 130 and 160). We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light for the first time by the investigations of the absorption spectra of solutions which have been carried on in this laboratory. Many of the phenomena which were thus explained, it seemed, could not be explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution, as proposed by Jones about a dozen years ago (*Am. Chem. Journ.*, 1900, xxiii., 89) to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions which we use in the laboratory, and not simply a theory of ideal solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form complex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The

fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favour of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficientiy great to show the phenomenon in question. We, therefore, do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing is shown by the results given in Table V. Here the solutions of the three salts in question that were used are more dilute than those for which the results are tabulated in Tables III. and IV. An examination of this table will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly what we would expect in terms of the solvate theory of solutions. The more concentrated the solution the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance, the more pronounced the phenomenon in question.

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium chloride. They, however, show in addition that water is more transparent in the region of 1·1 μ and more opaque at 1 μ. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerisation which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection that, while calcium chloride and magnesium chloride crystallise with only six molecules of water, and are, therefore, only largely hydrated, aluminium sulphate crystallises with 18 molecules of water, and is, therefore, very largely hydrated.

The results in Table VI. are, as has already been stated, the radiomicrometer deflections for a solution of aluminium sulphate and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water shows that the two are almost equally transparent to all the wave-lengths studied.

A comparison of aluminium sulphate with its corresponding water brings out the phenomenon that we are now discussing in a very pronounced manner. It is for this reason that the data in this paper are given.

One other relation of a general character should be pointed out. The curves upon all six of the figures show that the addition of salt to water shifts the absorption towards the longer wave-lengths. This is analogous to what has already been found by Jones and Uhler (Carnegie Institution of Washington, Publication No. 60), Jones and Anderson (*Ibid.*, Publication No. 110), Jones and Strong (*Ibid.*, Publications No. 130 and No. 160), and Guy and Jones (*Am. Chem. Journ.*, 1913, xlix., 1), when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and the increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We should naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the discovery made by Jones and Murray (*Am. Chem. Journ.*, 1903, xxx., 193), that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why non-hydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave-lengths. It may be that the effect of the dissolved substance in breaking down the association of the water is pronounced only in the case of water of hydration or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

In conclusion we wish to express our thanks to Professor A. H. Pfund, who has made many valuable suggestions during the progress of this work. We would also express our thanks to Dr. E. P. Wightman, who has kindly drawn the curves for us.

ALLOYS OF COBALT WITH CHROMIUM AND OTHER METALS.*

By ELWOOD HAYNES.

As in organic nature, certain animal and vegetable forms have undergone modifications, and thus, as it were, fitted themselves to live in a new environment, so it has been found possible in certain instances to form new metallic combinations which are practically immune to the natural conditions that exist on the earth at the present time. A few of the rare metals, such as gold, silver, and the metals of the platinum group, are found native, but the commoner heavy metals are nearly always found in the form of oxides or sulphides.

For a number of years I have made experiments with a view to finding certain metallic combinations of alloys which would not only resist oxidation and other harmful influences, but would also possess valuable physical properties, which would render them fit for special services. The first decisive step made in this direction was the discovery of an alloy of nickel and chromium in 1898. The properties of this alloy have already been described in a previous paper (*Journ. of Indus. and Eng. Chem.*, ii., 397). Immediately following the discovery of the nickel-chromium alloy, I produced an alloy of cobalt and chromium. This has likewise been described in the previous paper, but the range of proportion between the cobalt and chromium is so great, and the combination is modified to such a marked degree by the introduction of other substances, that I have felt justified in reading another paper on this subject, describing more fully my researches in this particular direction.

As early as 1907 and 1908, I made alloys or combinations of cobalt, chromium, and tungsten; cobalt, chromium, and molybdenum; and cobalt, chromium, tungsten, and molybdenum. I have made alloys of cobalt and chromium containing zirconium, tantalum, thorium, titanium, vanadium, &c. I have also added to the cobalt-chromium alloys the non-metallic elements, carbon, silicon, and boron. Some exceedingly interesting results have been obtained from these various combinations, and while further investigation is necessary in order to fully

* Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912. From the *Journal of Industrial and Engineering Chemistry*, v., No. 3.

determine their chemical and physical properties, a number of them have shown interesting economic possibilities.

The preliminary fusions were made in graphite crucibles by means of a furnace operated by natural gas. I was later obliged to use crucibles of a special composition, not only to avoid the contamination of the metal by carbon from the crucible, but also because they proved more reliable under long-continued heating than those made of graphite.

The metal tungsten alloys readily with chromium and cobalt in all proportions. When added in small quantity to the cobalt-chromium alloy, it seems to have little influence on the properties of the combinations, but if the proportion rises to 2 per cent or 3 per cent, a notable effect is produced. Generally speaking, the cobalt-chromium alloy becomes harder and more elastic, especially if it contains a small amount of carbon, boron, or silicon.

The following experiment shows the effect of melting the alloy in a graphite crucible:—90 grms. of cobalt, 6·3 grms. of tungsten, 18 grms. of chromium, together with a small quantity of calcium silicide, were introduced into a graphite crucible. The resulting alloy was very hard, and the crucible much eroded on the inside. The bar could be slightly flattened at one end, and after being made into a cold chisel, showed remarkable qualities. It would not only scratch glass, but also quartz crystal. It was quite tough at ordinary temperatures, and would cut small chips or shavings from a piece of stellite. At a bright yellow heat it showed signs of fusion, and became covered with a skin of oxide.

An alloy was made by melting the following in a special crucible:—Cobalt rondelles 80 grms., chromium 20 grms., tungsten 7 grms., calcium silicide 10 grms., calcium carbide 5 grms. As soon as the above were melted, the crucible cover was removed, and 15 grms. of an alloy of cobalt and boron were introduced. The crucible lid was then replaced and the heating continued. A heavy, thick slag formed, which was removed before pouring the metal. The resulting bar was very hard and *elastic*, but drew only slightly under the hammer, and then broke. A cold chisel made from the cast metal cut iron readily. The bar was broken up and remelted with about one-third of its weight of an alloy of cobalt, chromium, tungsten, and carbon. The result was a fine-grained alloy which was very *elastic*, and would draw out to a considerable degree under the hammer without checking. Its elastic limit must have been very high, since when it broke, the pieces were thrown violently.

Taking the alloy of chromium and cobalt as a basis, and holding the proportion of chromium at 15 per cent of the entire mixture, it was found that the alloy gradually increased in hardness with the percentage of tungsten. When the quantity of tungsten rises to 5 per cent, the alloy becomes distinctly harder, particularly when forged under the hammer. When the tungsten reaches 10 per cent, the metal still forges readily, and a tool formed from the alloy takes a fine cutting edge. This alloy is suitable for both cold chisels and wood-working tools. When the tungsten rises to 15 per cent, the metal can still be forged, but great care is necessary in order to avoid checking. The alloy is considerably harder than that containing 10 per cent of tungsten and is excellent for cold chisels. When the tungsten rises to 20 per cent, the alloy is still harder, and can be forged to a small extent. It makes good lathe tools for cutting steel and other metals at moderate speeds. When the tungsten rises to 25 per cent, a very hard alloy results, which cannot be forged to any extent, but casts readily into bars which may be ground to a suitable form for lathe tools. These tools have shown great capabilities, particularly for the turning of steel, since they are very strong, and retain their hardness at speeds which almost instantly destroy the cutting edge of a steel tool. The tungsten may be still further increased to 40 per cent, and the alloy will retain its cutting qualities, and for turning cast iron this alloy answers even better than that containing 25 per cent. When the tungsten reaches 40 per cent or more, the alloy becomes so hard that it will not only scratch glass, but will readily scratch quartz crystal. A small drill, made of this material, drilled a hole through the wall of a glass bottle without the addition of any liquid or other lubricant. A three-eighth inch square cast bar, when ground to a suitable edge, was set in a tool-holder attached to a lathe. The workman who had operated the lathe had been able to turn to form 26 cast iron wheels in 10 hours with a steel tool of the same size. The stellite tool turned 49 of these wheels to form in the same time. The steel tool was ground 50 times during the operation, while the edge of the stellite tool was dressed slightly by a carborundum whetstone, after its day's work was completed. A set of steel cutters, placed in the boring head of a cylinder-boring machine, were able to bore from 26 to 28 holes in ten hours. These cutters were replaced by others made of stellite, which performed the work in three hours and twenty minutes, or a little more than one-third the time. Not only was the speed of the mill doubled, but the feed also, and notwithstanding this severe ordeal, the stellite cutters were only slightly worn, while it would have been necessary to re-grind the steel cutters at least two or three times for the same service at slower speed. Some remarkable results were obtained in the turning of steel on the lathe. For example, a cylindrical bar of annealed nickel-chrome steel, about 2¼ inches in diameter, was placed in a lathe and turned with a steel tool at about as high a speed as the steel would permit without "burning." The steel tool was then replaced by one of stellite, and the speed at the same time increased to two and two-thirds its former speed. The stellite tool retained its edge under these severe conditions, and produced a shaving weighing one and two-tenths pounds in one-half minute. Just what the effect of the alloy will be in machine shop practice is at present somewhat difficult to determine. In my opinion, however, it will not fully supersede high-speed steel in the machine shop, but in cases where rapid work is the main consideration it will doubtless replace high-speed steel.

When molybdenum is added to a 15 per cent cobalt-chromium alloy, the alloy rapidly hardens as the molybdenum content increases, until the content of the latter metal reaches 40 per cent., when the alloy becomes exceedingly hard and brittle. It cuts keenly and deeply into glass, and scratches quartz crystal with ease. It takes a magnificent polish, which it retains under all conditions, and on account of its extreme hardness its surface is not readily scratched. When 25 per cent molybdenum is added to a 15 per cent chromium alloy, a fine-grained metal results, which scratches glass rather readily, and takes a strong keen edge. Its colour and lustre are magnificent, and it will doubtless find a wide application for fine hard cutlery. It cannot be forged, but casts readily, and its melting-point is not abnormally high.

If carbon, boron, or silicon be added to any of the above alloys, they are rendered much harder, though their effect is not always desirable, since they tend to render the alloys more brittle.

If either tungsten or molybdenum is added to a cobalt-chromium alloy containing 25 per cent of the latter metal, the hardness of the alloy is rapidly increased. When the percentage of tungsten, for example, reaches 5 per cent, the alloy can be readily forged, and forms an excellent combination for wood-cutting tools, such as chisels, pocket knives, &c. When molybdenum is added to the same mixture of chromium and cobalt, much the same effect is produced, though, generally speaking, a smaller quantity of molybdenum is required to produce a given increase in hardness. In some instances I have found it advisable to add both molybdenum and tungsten to the cobalt-chromium alloys. Generally, the colour and lustre of these alloys, after polishing, are magnificent, and they seem to resist atmospheric influences equally as well as the binary alloy of cobalt and chromium.

NOTES ON THE CHEMISTRY OF PAPER-MAKING.

By THOMAS J. KEENAN, F.C.S.

In an address before the King's County Pharmaceutical Society in the Brooklyn College of Pharmacy on January 14, 1913, the managing editor of *Paper* described some of the operations involved in the manufacture of woodpulp and paper, contrasting them with the work of the pharmaceutical chemist. He demonstrated among other things that the same uncertainty which formerly prevailed in pharmaceutical work—and which still exists to some extent—regarding the extractive or alkaloidal strength of the ultimate tincture or extract, is experienced by the papermaker in regard to the nature of the product he may obtain after extracting his wood and mixing the residuum with varying proportions of other materials, such as clay, alum, and rosin, in a beater—the modern analogue of the stamping machine or crude mortar and pestle of the mediæval craftsman.

The application of chemistry to papermaking began with the process of treating wood with caustic alkalis or alkaline earths so as to extract a product to replace the pulp made from rags. It had not been overlooked, of course, that the use of chlorine bleach came first, following the discovery of chlorine by Scheele in 1774.

The timber, from which the pulp or cellulose destined to form the finished sheet of paper is produced, varies in quality according to cultivation, soil, and climatic influences in much the same way as do the drug-producing plants, and the quality and quantity of pulp varies according to the class of woods used and the nature of the process, so that uniformity of product is nearly as difficult in the one case as in the other.

The production of a finished paper of uniform and unvarying quality and characteristics, as determined by chemical and microscopical tests, is impracticable, owing to conditions inherent in the process of manufacture. The papermaker cannot tell to a nicety what proportion of the materials which go to make up his "furnish" or formula will be retained in the ultimate paper and what will go out with the water which is drained away from the pulp as it travels on the running wire of the paper machine to the press and drying rolls. In this respect the art of papermaking has not kept pace with the progress of other arts and crafts, though in the direction of mechanical improvements there are few industries in which mechanical invention has been so highly developed or in which engineering as a science plays a more important part, some of the special machinery in the equipment of a modern paper mill being examples of engineering skill that are little short of marvellous in the ingenuity of their construction and operation.

In the primary processes of separating the pulp or cellulose from the wood the pharmacist will see no analogy with any operation known to his art. On the contrary, he will observe methods employed and results obtained as astounding by their destructive wastefulness as by total opposition to galenical methods in the extraction of valuable plant constituents. It is in the intermediate and later stages of papermaking—in the combining of the "furnish," as the assembled ingredients of the formula for a given paper are conveniently termed, and in the testing of papers—that he will note familiar combinations and reactions.

The simplest form of woodpulp, that known as "ground wood," which forms the body of newsprint paper, is produced by pressing logs of cone-bearing trees, such as spruce, balsam, pine, and fir, freed from bark, and cut into short pieces about two feet long, against revolving grindstones, under a stream of water, so that the disintegrated pulpy fibres, torn away from the log, obliquely or against the grain, can be run off into tanks and thence flowed away to undergo a screening and straining operation for the removal of refuse and unground lumps. As the pulp obtained in this way contains the sap, lignin, and resin of the raw wood, substances that are prone to rapid oxidation and discoloration, paper made from it soon deteriorates, becoming brown and brittle, and it is a very perishable product. Pulp of this kind, however, is only used as an admixture with chemically prepared pulp in the manufacture of newsprint and the cheaper grades of book paper, or alone in the manufacture of boards; ground poplar wood being also used to some extent for this purpose.

It is the pulp produced by chemical means which has most interest for the pharmacist, the systems in use being, as already indicated, so much at variance with pharmaceutical work and especially the extractive processes employed in pharmacy. The chief processes are known as the sulphite, the soda, and the sulphate. By the solvent action of the chemical solutions upon the non-fibrous constituents of the wood the cellulose is set free from its enveloping bodies and is recovered to the extent of nearly 50 per cent of the total weight of the wood. The material which is extracted, consisting of all the soluble constituents of the wood—the gums, resins, tannins, and other valuable plant principles which encrust the cellulose—represents to the papermaker so much offal or waste, and, in the soda process, is destroyed by burning, the soda being recovered; and, in the sulphite process, washed into rivers and streams, with a total loss of organic extractives and chemicals.

It is scarcely necessary to emphasise more particularly the sharpness of the contrast that is here presented to the work of the pharmacist, where the end aimed at is the separation of the active and soluble constituents of the plants from the inert insoluble portion; the residue or marc, consisting of broken down weedy tissue and fibres, being rejected. But to illustrate better the contrast in work, a brief description of the sulphite process of pulp-making may be given. The wood, having been cleaned and cut up into pieces from two to five feet in length, as in the ground wood process, is chipped up into small pieces or chips about one-fourth inch to one-half inch thick and boiled under pressure in large steel digesters capable of holding twenty tons of wood at one operation and yielding ten tons of finished pulp. The digesters are lined with heavy cement backing faced with brick, pointed with litharge and glycerin, to prevent contact with the metal.

The sulphite liquor in which the wood is boiled is made by passing sulphur dioxide—obtained by burning sulphur, or iron pyrite, in special ovens—into tanks filled with water and a known quantity of slaked lime (prepared from dolomite). This results in the formation of a solution of the acid sulphites of calcium and magnesium, which is the active solvent agent. The chemistry of the reaction between the wood and the sulphite liquor prepared from dolomite or magnesian limestone is tersely but sufficiently stated by Thorp ("Outlines of Industrial Chemistry," Macmillan, 1911), who explains that the acid sulphites react much like sulphurous acid, but the sulphites combine with the aldehydes formed in the first stages of the decomposition, producing stable and soluble double salts. The organic acids which are also formed decompose the bisulphites and form soluble calcium and magnesium salts, while the sulphurous acid gas is set free, causing a constant increase of pressure within the digester. The acid sulphites also tend to bleach the colouring matter of the fibres by forming colourless compounds with them, but this is a very unstable bleach and the original colour soon returns when the pulp is made into paper. Bisulphite of calcium is unstable and decomposes readily into neutral sulphite, setting free sulphurous acid. This results in the precipitation of the neutral sulphite on the fibre, which is left harsh even after long washing. Magnesium bisulphite is more stable, and although less corrosive to the fibre, it dissolves the non-cellulose matter even more completely than does the lime salt; further, any sulphate or neutral sulphite which may be formed is easily washed off and the pulp is left soft and white. Sodium bisulphite gives a better product than either of the foregoing, and strong

liquors can be made from it; but it is too expensive for general use.

When the digesters have been filled with the wood chips and the requisite quantity of sulphite liquor is added, the manhole or cover at the top of the digester is securely fastened, and steam is turned on gradually until the pressure reaches seventy or eighty pounds. The cooking is steadily maintained at this pressure for a period of eight to ten hours. At the end of this time the contents of the boiler, consisting of softened pulp, are discharged into large vats and washed. The spent liquor containing the dissolved resinous and non-fibrous portions of the original wood is allowed to drain away from the mass in the tank, which is then washed out and made ready for another charge.

It is the disposition of this spent liquor which constitutes one of the weightiest problems confronting the manufacture of chemical pulps to-day. He is eager to be informed of a means of utilising the liquor that would obviate the present necessity of throwing it into contiguous rivers and streams, for he realises the danger that threatens the industry from the enactment of laws that will prevent him from turning his waste liquors into the watercourses of the country in such large quantities as has been done up to the present time.

By neutralising the liquor and starting fermentation of the contained sugars, alcohol of a low grade is produced from it in several pulp plants in Sweden, and by a patented concentration process used in the United States, a compound is formed from the liquor, named glutrin, which is utilised as a binder in roadmaking, as a tanning extract, and as an adhesive for sand in making moulds and cores for iron castings in foundries.

But the profitable recovery of the organic matter dissolved from wood in the sulphite process is still an unsolved problem. The recovery of the innumerable organic substances dissolved in it, which is so fascinating a field of speculation for the chemist, has no interest for the pulp-maker, and is regarded as something of minor importance compared with the question of getting rid of the liquor in some way agreeable to the authorities and at the same time inexpensively and expeditiously. Although the problem has been deeply studied by able chemists for the past twenty years, it has yet to be tackled by a pharmaceutical chemist, and when it is we may look for the production of a whole series of new organic compounds.

In the soda and the sulphate processes of extraction there is effected a partial recovery of materials. By incinerating the spent soda liquor, after evaporating and concentrating it, the soda itself is regenerated, but there is here again a total loss of the organic derivatives of the wood, which are burned up in recovering the soda.

The soda process is used for soft woods like poplar, cotton, and basswood, whereas the sulphite procsss is exclusively employed for coniferous woods. The chipped wood is boiled in a solution of caustic soda for eight or nine hours at a pressure of seventy or eighty pounds. The pulp produced is soft and bleaches well, making it especially well adapted for the manufacture of book and magazine papers.

Sulphate pulp is prepared by boiling the wood chips in a solution of sodium sulphate containing some caustic soda and sodium carbonate. It is a slower process than either the sulphite or the soda, as the period of boiling, instead of being eight or nine hours, is sometimes extended to thirty-five hours, though good results are possible with a shorter cooking. The sulphate is reduced to sulphide by organic matter during incineration as a step in recovery, and by its presence in the liquor subsequently made oxidation of the fibre is prevented, so that a good yield of strong fibre is obtained. The so-called kraft papers are made by this process, which is not a popular one, as the gases formed have a very offensive odour, which affect the whole neighbourhood of the mill and make the atmosphere almost unendurable to human beings and incapable of supporting plant or vegetable life.

Some of the technical operations of the papermaker afford abundant opportunity for exercise of galenical ingenuity and skill, as, for example, in the sizing of paper to give it a surface resistance to the penetration of liquids like ink, so that the paper may be written or printed on without the ink spreading over the sheet.

In the sizing of newsprint and the common grades of book paper the sizing substance is the ordinary rosin of commerce, which is added in the form of rosin soap to the pulp mass of fibres in the final stages of beating, and precipitated by alum, after the proper proportion of kaolin or china clay has been added (from 5 to 15 per cent) and the yellowish colour of the ground wood has been toned up by the addition of sufficient blue and red aniline dyes or other colours required to impart a white appearance to the finished sheet of paper. In order to insure the perfect distribution of the rosin throughout the paper pulp it is introduced as a liquid soap, made by boiling rosin with soda-ash and adding water, the following being a typical formula :—

Rosin	1350 lbs.
Soda-ash	165 lbs.

Boil for about four hours and just before boiling is completed add about thirty gallons of water. Strain through a No. 80 sieve.

A definite quantity of the soapy emulsion of rosin thus formed is mixed with the contents of the beater, and when it is well distributed, alum is added in sufficient quantity to salt out the rosin and take with it for precipitation into the fibres of the paper pulp the kaolin and other ingredients of the furnish.

It is a disputed question in paper chemistry whether the alum simply throws the rosin out of solution, salts it out, as it were, or combines with it to some extent to form an aluminium resinate. The weight of authority leans to the conclusion that no chemical combination takes place, good results in sizing with rosin having been obtained by the substitution of magnesium sulphate, or diluted sulphuric acid, for alum. At best the salting out process as ordinarily practised is not distinguished by scientific precision, and much more alum appears to be used than is necessary. Alum and rosin when present in excessive amounts cause paper to turn a brownish colour, and it gradually becomes brittle and disintegrates in consequence of the formation of free acids and other chemical changes.

The supply of rosin is not inexhaustible and some scarcity has already developed, and as a consequence of this and a corresponding advance in price, the papermakers are casting about for cheaper substitutes. Besides experimenting with the waste rosins of the rubber industry, an attempt has been made to revive the ancient use of starch as a sizing material, with a fair measure of success as regards ordinary printing papers, but unsuccessfully in the case of writing papers, which require to be almost waterproof in their ink resistance. In this process a compound of starch and aluminium silicate is deposited in the fibres by combining in a cooking operation a partially gelatinised starch with sodium silicate and salting out the mixture with aluminium sulphate.

The more expensive handmade papers are sized with a solution of gelatin, the sheets being dipped separately into a tub of the size and afterward hung up to dry, being finally pressed between zinc plates. In another process now more generally used the sheets of paper are carried by travelling felts through a bath of heated size, the excess gelatin being removed by the action of rubber or wooden rollers through which the papers are passed before leaving the apparatus, and the drying is effected on an extension of the machine. With the ordinary machine-made writing paper, however, the sizing material is mixed with the pulp in the beating engine, as in the case of newsprint and book paper, and there interlocked with the fibres by the alum salting out process previously described.

It is expected of the pharmacist that he should be well informed regarding methods of determining the quality of

paper by microscopical and chemical tests at least—physical methods may be left to the experienced paper-maker or dealer, who is often able to make a shrewd guess at the composition of a paper by the mere appearance and feel of the finished product.

In "taking the fibre count," as the method of estimating the proportion of pulps in a paper is termed, the use of a staining agent is necessary, all vegetable fibres being transparent and nearly colourless. The best stain for this purpose is Herzberg's chlorzinciodine solution, which is made up as follows:—

Solution A.

Zinc chloride	20 grms.
Distilled water	10 cc.

Dissolve.

Solution B.

Potassium iodide	2·1 grms.
Iodine crystals	0·1 ,,
Distilled water	5·0 cc.

Dissolve.

Dissolve A by adding the water to the zinc chloride in a beaker.

Dissolve B by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 cc. of water.

The two solutions—A and B—are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off into amber glass bottles fitted with dropping stoppers.

A drop of Herzberg's stain applied to the paper pulp on a microscope slide brings out a wine-red colour on cotton and linen fibres, gives a good clear blue colour with bleached soda and sulphite woodpulps and a characteristic yellow or greenish grey-yellow with ground or mechanical woodpulp.

The following method of preparing a sample of paper for the microscope is used by the Bureau of Standards, Washington, D.C.:—

Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a beaker and covered with some ½ per cent caustic soda solution, and the whole mass is then brought to a boiling over a suitable heating device. After boiling for about a minute some tap water is added to wash out the caustic soda, followed by two or three drops of a 25 per cent solution of hydrochloric acid to neutralise the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper are pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test-tube and the test-tube half filled with water. The test-tube is then shaken vigorously until the paper has been entirely broken up and the fibres are well separated. A small portion of the pulp is then carefully removed on the point of the microscope needle from the test-tube and placed on each end of one of the microscope slides, the excess liquid being removed by a pointed strip of filter paper brought in contact with the edge of the drop.

The fibres forming the pulp are thoroughly dried and a drop of the Herzberg stain is added, then the fibres are well "teased" out by the use of the microscope needles, a cover glass is placed over them and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper.

The slide is next placed under the microscope, and after studying the various fields an estimate of the proportion of each of the various kinds of fibres may be given.

One of the most frequently used solutions for staining fibres for microscopic examination is a solution of iodine in potassium iodide of the following composition:—

Iodine	1·15 grm.
Glycerin	1·0 ,,
Potassium iodide	2·0 ,,
Water	20·0 ,,

In contact with this solution cotton, linen, bleached hemp, and ramie fibres are coloured brown; while mechanical woodpulp, jute, and manilla hemp are coloured yellow or yellow-brown. Chemical pulp of wood, straw, and esparto are not affected.

A solution of calcium nitrate in iodo-potassium iodide is said to offer some advantages over chlorzinciodine solution. For one thing it does not absorb moisture from the air, and it does not alter the fibres. It is made as follows:—

Solution No. 1.

Nitrate of calcium crystals ..	100 grms.
Distilled water..	50 ,,

Dissolve.

Solution No. 2.

Iodine	1 grm.
Potassium iodide	5 ,,
Distilled water..	90 ,,

Dissolve.

For use 3 cc. of Solution No. 1 is added to Solution No. 2.

This solution stains linen fibre a rose colour with a brownish tinge; ground wood is coloured yellow; bleached sulphite fibre, a delicate rose tint; unbleached sulphite fibre, clear yellow; soda poplar fibre, indigo blue; straw fibre and esparto blue.

Several rough identity or diagnostic tests for the presence of ground wood in paper are employed by paper dealers, of which the following may be noted:—

A solution of phloroglucin in alcohol is used for identifying mechanical or woodpulp, which turns a beautiful red colour in contact with the reagent, the depth of tint, as compared with Schopper's standard colour tables, corresponding to the amount of mechanical pulp, or lignified fibre, present. The procedure is as follows:—

Into a flat porcelain dish pour 2 parts of a 2 per cent alcoholic solution of phloroglucin and 1 part of hydrochloric acid (phloroglucin, 1 grm.; alcohol, 50 cc.; hydrochloric acid, 25 cc.), and immerse in the solution the paper under examination. After ten minutes of contact compare the colour developed with Schopper's standard colour table.

In papers having a red or rose colour the phloroglucin reaction breaks down and the employment of benzidine hydrochloride is recommended, this reagent giving rise to an orange colour in the presence of mechanical woodpulp. The reagent is made by rubbing up 15 grains of chemically pure benzidine with 15 minims of hydrochloric acid and dissolving the benzidine hydrochloride formed in 2½ drms. of water at 122° F. The solution is simply dabbed on the paper to be tested, and the orange colour produced in the presence of mechanical woodpulp is the more intensive the more woodpulp is contained in the paper. The test is a very delicate one, the orange colour being produced even when only traces of mechanical woodpulp are present.

Aniline sulphate stains lignified fibre yellow, and a 10 per cent solution of this salt, acidulated with sulphuric acid, imparts a golden yellow tint to paper containing ground wood, the colour being more or less intense according to the proportion of ground woodpulp present. A solution of aniline chloride and hydrochloric acid is also used, but the results with each of these aniline solutions are inferior to those obtained with phloroglucin.

Wurster's reagent is popular in Germany as a diagnostic test for ground woodpulp, but as it, as well as phloroglucin and the aniline salts, develop their characteristic colours with any lignified fibre, the test is not conclusive of the presence of ground woodpulp alone. Wurster's reagent consists of a 50 per cent solution of dimethylparaphenylenediamide in water. It gives a deep red colour

with ground woodpulp. There are now available test-papers impregnated with Wurster's reagent which are called "di-paper" for convenience. Strips of this test-paper are placed in a double sheet between the paper to be tested. After moistening the layers of paper with water the red colour that develops is compared with a standard table of colour values which is sold with the test-papers.

It is the lignocelluloses, reacting to the foregoing reagents, which impart the greatest element of weakness and decay to paper. They are unsaturated compounds greedy of oxygen and profoundly affected by all oxidising agents. Pure cellulose is a saturated compound which is resistant to the action of both chemicals and atmospheric changes, and this accounts for the practical indestructibility of rag papers, which are free from lignin, and consist of nearly pure cellulose. Books and papers dating from the middle ages are to be found in museums and libraries to-day in a good state of preservation because they were made at a time when rags were the only crude material for the manufacture of paper.—*The Chemical Engineer*, xviii., No. 4 (from *Paper*).

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

Keep Your Fluorine as Long as Possible.

Professor Armand Gautier has continued the explanation of the researches that, in collaboration with M. Clausmann, he has undertaken concerning the fluorine in the organism.

The authors have discovered that for 100 grms. of substance there exists 3·04 mgrms. of fluorine in the brain of a man; in the brain of an ox 3·46 mgrms.; in the human lungs, 2·44; in the thymus of a young lamb, 8·48; in the kidney of a man, 2·30, &c. These quantities, although very weak, are sufficient to explain the rôle of the fluorine, which, as M. Armand Gautier established recently, is necessary for the assimilation of phosphorus. These last experiments have likewise confirmed this remark that fluorine diminishes as the organism grows older.

Pieces of Money and Hygiene.

In order to avoid disputes, most of the tramcar and autobus conductors have a habit of holding, between their teeth, the coins for which they have to give change. The Council of Hygiene of Rome has received many complaints concerning this habit, and certain experiments, tried under its direction, have shown, it appears, that if banknotes are laden with bacteria, the copper, silver, and gold coins are practically *aseptic*, on account of the bactericidal action of the metallic salts and oxides formed on their surface. On the other hand, it was declared that nickel coins did not enjoy this same property precisely on account of their unalterability.

But the conclusions of the learned Italians are not accepted in France. M. Langlois, Director of Science, has washed several pieces of money, more or less worn, in a determined quantity of sterilised water, and the averages of his numerations for each series of coins have reached the following figures for each cubic centimetre of the washing water:—

10 c. Copper coins,	760,000	bacteria,	3	p.c.	mould.
25 c. Nickel „	140,000	„	2	„	„
2 fr. Silver „	160,000	„	1	„	„
25 fr. Gold „	220,000	„	0	„	„
Banknotes ..	1,200,000	„	8	„	„

Among the bacteria the most frequently met with are—Sarcines, Bacillis subtilis, Staphylococcus, Pneumobacillus, Bacillus liquefaciens; amongst the moulds by the side of diverse Penicillium, the terrible Aspergillus niger.

The experiments of M. Langlois indicate that if pieces of money constitute a bad centre of culture for bacteria, they transport, nevertheless, very dangerous species in alarming numbers.

The adoption of nickel money constitutes a very appreciable progress, since the washings of several pieces of 25 c. gave the lowest average. On the other hand, the banknotes are particularly rich in bacteria.

The water in which had been washed a very much worn French fifty franc banknote supplied more than three millions of microbes. That used for washing a nearly thousand franc banknote gave only 270,000.

A Mammoth in Flesh and Bones.

"L'Anthropologie," by the pen of its director, Professor Boule, informs us of the precious acquisition just made by the Paris Natural History Museum of a mammoth with its soft parts partially preserved. This magnificent example has been offered to the Museum by Count Stenbock-Fermor, who had it extracted at his own expense from one of the islands of New Siberia, and brought it to Europe by sledge, boat, and railway. It is probably the only example that will ever be seen in central Europe, for subsequently to the gift of Count Stenbock-Fermor an imperial ukase has forbidden any further exportation of mammoths either whole or in parts.

It is known that these fossils preserved in the ice were perceived in 1806 (Adam, Mouth of Lena), but the only mammoth preserved in these conditions and brought to Europe is to be seen in the Museum of the Academy of Science of St. Petersburg. The anatomy of the soft parts, its histology, the study of the blood, have constituted, on the part of the Russian *savants*, a palæontological work of a kind evidently quite new, presenting, at least, a lively interest of curiosity.

The sample at the Paris Museum of Natural History is sufficiently well preserved to allow of like studies. They are already begun.

The whole animal and its soft parts will shortly be exposed to the public; it will form a new attraction to the great scientific establishment. The public will doubtlessly contemplate with a lively interest, besides the skeleton, of which the skull notably is perfectly preserved, a large part of the skin covered with its hair, the tail, and a whole ear.

Vegetables Manufacture Urea.

Urea has long been considered as characteristic of the desassimilation of animal albuminoids. However, there has been some found in mushrooms. Recently, M. Fosse in analysing a rather large number of vegetables, has remarked that urea is to be met with very generally in the vegetable kingdom—carrots and potatoes. What is to be deduced from this presence of urea? Can it be considered as a physiological product of the vegetable cell, or has it simply been drawn by the roots from the soil where it is always to be met with in more or less important quantities?

The experiments have shown that it could really be considered as a product of the activity of the vegetables cells. By cultivating moulds such as *Aspergillus niger* and *Penicillium glaucum* in aseptic conditions and on definite media containing sugar and ammonia, it has been stated that these moulds really produced urea. Likewise, in treating the higher classes of vegetables, wheat, barley, Indian corn, peas, clover, and beans, M. Fosse has been able to show that in these plants also urea was formed in the course of germination, when the embryo then growing consumes the reserve material contained in the grain. Like animals, vegetables are then susceptible of producing urea.

The Survival of Congealed Fish.

The experiments performed some time ago by Professor Raoul Pictet have shown that living fish might be con-

gealed without being killed, provided that the freezing process was performed in a very slow manner. When the fish is fixed in the block of ice, it is noticed that its tissues can be pounded as ice is pounded. If at the end of a certain time the block of ice is thawed very slowly, it is remarked that when the water is melted, the fish gradually regained their activity, and after some time they swim about as if nothing had happened.

It is in taking these facts as a basis that MM. Mir and Audigé have established the principle of a process by which it is possible to transport to a distance fish living but congealed. The blocks of ice containing the congealed fish could be transported in frigorific wagons at 0°.

This process is much more economical than that which exists on certain railways, notably in Germany and Austria, and which consists in transporting the living fish in water. In this case it is necessary to employ a relatively large quantity of water. To transport one kilogrm. of carp, four or five litres of water are required, and for the same weight of trout from 10 to 20 litres of water are necessary. A wagon that can only carry 10,000 kilogrms. would be able to transport only 500 to 1000 living trout.

The process indicated above by MM. Mir and Audigé is infinitely more simple and less costly. It cannot fail to interest the hygienist.

The Synthesis of Vegetable Matter.

M. Daniel Berthelot, Professor at the Higher School of Pharmacy, and M. Gaudichon have just communicated to the Academy of Sciences the continuation of their researches on the synthesis of vegetable matter by light, thanks to the gases of the air. By exposing carbonic acid and the amount of water contained in the atmosphere to the ultra violet irradiation of the mercury lamp they have obtained both formic acid, the simplest of vegetable acids, and formaldehyde, which is the point of departure of sweet matters and of celluloses.

These reactions which take place in plants, in the sun, only under the influence of diastases, is realised here in vitro, thanks to the accelerating catalytic power of the ultra-violet light.

The Action of Ultra-Violet Rays.

Professor Hunneguy has presented before the Academy of Sciences a very interesting note concerning the action of ultra-violet rays on the development of the egg of the "Ascaris" or Ascarides.

We are acquainted with the first manifestations of life only from the observation of the eggs of the lower animal life. As soon as it is fertilised the egg is segmented into two parts, then into four, then eight, and so on. The ultra-violet rays slacken this segmentation of the egg, and this slackening is proportional to the quantity of energy received.

Interesting Grafting.

In a certain number of cases (18 out of 100 trials) M. Daniel has managed to graft the root of a carrot on to the root of another umbelliferous plant, the peppery fennel.

The carrot (a semi-red Nantes type) has a tuberculous red root, giving out a special smell and having a sweet taste. The peppery fennel has a white root, not very sweet, with a special smell and a pungent peppery taste.

The roots of the grafted carrots became tuberculised, their colour was red but mixed frequently with green or brown. So then the colouring of the grafted tubercle was modified, but, on the other hand, the red pigment of the carrot did not pass into the fennel.

The smell of the grafted carrots was also modified; moreover they were not so sweet, and had, though in a less degree, the taste of the root of the fennel. The carrot thus loses its alimentary value. What is interesting to note is that the exchanges between the graft and the subject are localised to such and such a substance and are not produced in the same manner on both sides.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume VII. Fourth Edition. Edited by W. A. Davis, B.Sc., A.C.G.I., and Samuel S. Sadtler, S.B. London: J. and A. Churchill. 1913.

The seventh volume of the fourth edition of "Allen's Commercial Organic Analysis" deals with the Vegetable Alkaloids, Glucosides, Animal Bases, and Acids, &c. As our knowledge of these subjects has rapidly advanced in recent years the text has had to be thoroughly revised, and many amplifications and corrections have been made. As far as possible the old arrangement and classification have been preserved. The section on Animal Bases, which has been re-written, and which gives an admirable survey of the analytical methods employed in their identification, is from the pen of Prof. A. E. Taylor, of the University of Pennsylvania.

Lectures on Chemistry in Gas-works. By W. J. A. Butterfield. London: The Institute of Chemistry of Great Britain and Ireland. 1913.

The two lectures which this booklet contains were delivered before the Institute of Chemistry in December and January, 1912-13, and were intended to give students and gas-works' chemists some idea of the nature of the work which they should be qualified to perform. The first lecture dealt with the requirements of a public gas supply, the consumption of gas in different countries and cities, and the evolution of modern methods of gas making from the earliest processes. In the second lecture the lecturer discussed the cleaning of gas, the recovery of nitrogenous products from coal, and the chief by-products. The analytical work which the gas-works' chemist will be called upon to carry out is outlined, and a high ideal of efficiency, alertness, and skill is put before him; in the lecturer's opinion he should be possessed of a special knowledge of the chemistry of fuels, and in addition should have a thorough acquaintance with the principles of mechanics and physics.

Über die Aufnahme der Radium—Emanation durch das Blut. ("The Absorption of Radium Emanation by the Blood"). By C. Ramsauer and H. Holthusen. Heidelberg: Carl Winter. 1913.

The research described in this monograph was performed at the Radiological Institute attached to the University of Heidelberg, and has brought to light some facts of first-rate importance in medical and biological science. By means of a new method of measuring the absorption co-efficients of the blood for radium emanation it has been definitely proved that the coefficient is double that of water at the same temperature; thus some of the very contradictory statements to be found in literature may at last be regarded as conclusively refuted. It has also been proved that the red blood corpuscles are the chief carriers of the emanation, and the validity of Henry's Law has been established between very wide limits.

Handbuch der Arbeitsmethoden in der Anorganischen Chemie. ("Handbook of Practical Methods of Inorganic Chemistry"). Edited by Dr. Arthur Stahler. Volume I. Leipzig: Veit and Co. 1913. (M. 25).

Directors of laboratories and chemical demonstrators will find in this book much information which will be of great value to them. It is not always easy to obtain details of the latest forms of apparatus and of the best methods of carrying out special operations, such as are to be found here, and the text-books hitherto existing have not attempted to attain to the comprehensiveness at which the many collaborators who have written this book have aimed. In Volume I. the laboratory and its equipment are described, with illustrations of many kinds of apparatus, including the latest modifications and improvements.

Mechanical operations such as separation by filtration, centrifugation, &c., are also described, and valuable sections deal with the preparation and fitting up of apparatus and the making and storing of reagents. The actions of reagents on glass and the advantages of the use of quartz and other glasses are discussed. The section on the electrical apparatus employed in chemical work will be found exceedingly useful, providing as it does enough details for all ordinary purposes.

Die Gasglühlichtbeleuchtung in ihrer Entwicklung und Bedeutung. ("Incandescent Gas Lighting: Its Development and Importance"). By Dr. C. Richard Böhm. Charlottenburg: Gustav Heydenreich. 1913.

This little pamphlet has been re-written for the general public, and aims at giving a brief readable account of the use of the incandescent mantle in lighting by gas. Interesting details and illustrations of the first gas works built in 1825 in Berlin are given, and the evolution of the incandescent burner is traced. Those who are interested in questions of illumination will find that the pamphlet contains matter relating to the efficiency and expense of different systems which is worthy of their attention.

CORRESPONDENCE.

ATICONIC ACID.

To the Editor of the Chemical News.

Sir,—We have sometimes wondered why discoveries in science find their way so slowly into the text-books. As an illustration, in 1893 Dr. Arthur Brooke, in collaboration with Prof. Rudolph Fittig, in the Chemical Laboratory of the University of Strassburg, discovered a new isomeric unsaturated acid, to which they gave the name *aticonic*, because it more closely resembles itaconic acid than it does the other isomers, mesaconic and citraconic. This was considered at the time quite a brilliant and important discovery, and it received due consideration in the *Annalen* and other journals during the year in which the synthesis was effected.

In the summer of 1894, Prof. Fittig was honoured with an invitation by the German Chemical Society to read a paper descriptive of his work on the unsaturated acids, and naturally the newly discovered one was given prominent attention. The full text of this address was published in the *Berichte* of September, 1894.

An examination of fifteen or eighteen recent text-books on organic chemistry failed to show any mention of aticonic acid, although the other three isomers were described. These were German, English, and American works. One author of a widely used and well known text book, when his attention was called to the omission, said that in a brief work one could not include everything, and so he omitted aticonic acid, although he gave the other three a prominent place.

Is it possible that our text-book writers copy from each other, and do not sufficiently consider the original sources? —I am, &c.,

Nicholas Knight.

Cornell College, Mount Vernon, Iowa, July 9, 1913.

Literary Intelligence.—Messrs. J. and A. Churchill, of 7, Great Marlborough Street, W., have nearly ready for publication the Seventh Edition of "The Microtomist's Vade-mecum," by A. Bolles Lee; the Sixth Edition of the late Prof. Campbell Brown's "Practical Chemistry," edited by Dr. Bengough; and the Third Edition of a Text-book of Physics," edited by A. Wilmer Duff.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [1.], No. 6, 1913.

Polyazoxy Compounds.—A. Angeli.—When Mills's diazobenzene, $C_6H_5N_2.C_6H_4.N_2.C_6H_5$, is suspended in glacial acetic acid and heated on the water-bath with 30 per cent hydrogen peroxide, a bisazoxybenzene of formula $C_6H_5.N=N.C_6H_4.N=N.C_6H_5$ (with O above each N) is obtained. The azoxy compound, $C_6H_5.N_2.C_6H_4.N_2O.C_6H_4.N_2.C_6H_5$, is prepared by acting with sodium alcoholate on paranitrobenzene. It yields triazoxybenzene when treated with H_2O_2. Following are the characteristic properties of the three azoxy compounds:—

Azoxybenzene—Melting-point, 36°; colour, light yellow; coloration with H_2SO_4 at 100°, orange-red; with Br gives bromo-derivative.

Bisazoxybenzene—Melting-point, 155°; Colour, dark yellow; coloration with H_2SO_4 at 100°, violet; with Br gives dibromo-derivative.

Triazoxybenzene—Melting-point, 230°; colour, golden yellow; coloration with H_2SO_4 at 100°, blue; with Br gives dibromo-derivative.

Vol. xxii., [1], No. 7, 1913.

Electrolysis of Crystalline Compounds.—G. Bruni and G. Scarpa.—The authors have studied the electrolysis of silver iodide, using silver electrodes, and by six experiments performed at different temperatures, viz., 160°, 200°, 250°, 300°, and 400° (two experiments), have proved that the quantity of silver which migrates from the anode to the cathode follows Faraday's Law.

Hydrogenation of Santonine in Presence of Palladium Black.—G. Bargellini.—In presence of palladium black santonine, when it absorbs the quantity of hydrogen calculated for 2 atoms, is transformed into a dihydrosantonine, which with alcoholic potash gives a yellow coloration and a green fluorescence. This compound has a ketonic character, and yields a semicarbazone. When santonine, in presence of palladium black, absorbs the quantity of hydrogen calculated for 4 atoms it is converted into a tetrahydrosantonine, which yields no coloration with alcoholic potash. At the ordinary temperature and at a pressure of about an atmosphere santonine does not absorb more than 4 atoms of hydrogen.

MISCELLANEOUS.

Three New Alloys.—In their last official report as chemists to the American Institute of Metals, Arthur D. Little, Inc., of Boston, mention three new alloys among the various items of recent progress in the metal industry. A French patent has recently been issued covering the production of two types of alloys from copper, zinc, and silicon, which are claimed to possess great tenacity, resistance to acids and alkalis, and to be capable of rolling into finished shapes. Another new alloy has been patented by the Ajax Metal Company, composed of iron, nickel, and copper, which is claimed to be non-corrosive, malleable, of great tensile strength, and capable of being rolled, drawn, or cast. A new type of pyrophoric alloy has been patented in Germany which consists of the addition of 5 per cent metallic cerium to an alloy of manganese and antimony. The inventor claims excellent pyrophoric properties from this alloy, which is essentially different from the other alloys of this type in which cerium is the main source of the pyrophoric characteristics.—*Chemical Engineer*, xvii., No. 4.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2801.

THE CHEMICAL AFFINITIES OF NITROGEN.

By GEOFFREY MARTIN, Ph.D., M.Sc., B.Sc.

Nitrogen has long been regarded as an element possessed of very feeble affinities, and consequently the recent remarkable experiments of Strutt and collaborators on "Chemically Active Nitrogen" (*Proc. Roy. Soc.*, 1911, A, lxxxv., 219, 377; lxxxvi., 56, 262; lxxxvii., 179; *Nature*, May 15, 1913, p. 283), which revealed the possibility of nitrogen possessing strong affinities, came as a very surprising result to many chemists.

It seems, however, to be quite overlooked that the present writer no less than eight years ago in his book "Researches on the Affinities of the Elements" (published by Churchill, 1905), showed from a study of the affinities of the successive elements of the periodic system that nitrogen, owing to its position in the periodic system, must possess very strong affinities.

This result was arrived at by studying the manner in which the affinities of the successive elements altered as we went down the series Li, Be, B, C, N, O, F, and the writer then finally concluded that it is quite incorrect to speak of chemically active and inactive elements, but that practically all the elements investigated have their strong and weak affinities, only sometimes these strong affinities are exerted on well known elements—when we call the element "chemically active"—and sometimes on rare elements—when we call the element "inactive."

As the result of the study of the compounds of nitrogen and the compounds of neighbouring elements the writer showed that nitrogen, just like sodium or chlorine, possesses very strong affinities for some elements and very weak ones for other elements, but that its affinities were masked by three causes:—

(1) The elements for which it exhibits its strongest affinities are those which have the power of self-combination most strongly developed.
(2) That nitrogen itself has the power of self-combination strongly developed.
(3) That the elements for which nitrogen exhibits its maximum affinities are all somewhat uncommon in a chemical laboratory, and so the chemical activities of nitrogen are not brought prominently before the eyes of chemists.

All these causes *lower* the apparent power of entering into chemical combination of nitrogen, and have led chemists to almost universally regard nitrogen as very inert chemically.

Strutt's experiments revealing the chemical activity of nitrogen are, in fact, a remarkable fresh confirmation of the properties that I showed nitrogen to possess some eight years ago, and as Dr. Strutt refers back to Faraday (*Nature*, May 15, 1913, p. 285) for a vague prophesy in this direction, and appears to be quite unaware of my own results—arrived at by means of a laborious study of known compounds—I think that I can justly claim that I was the first who showed that *from its position in the periodic system* nitrogen *must* be an element possessing strong affinities, and also simultaneously clearly indicating what elements these affinities would be most strongly exerted upon.

As these results of mine appear to have been quite overlooked by current writers, and have considerable interest at the present time when atmospheric nitrogen is being fixed on an enormous scale commercially, I venture to bring my results once more before the chemical world.

The following is my method of investigating the magnitude and nature of the affinities which the elements Li, Be, B, C, N, O, F, exhibit in succession for the other elements of the periodic system. First of all I construct the periodic system of elements in the usual way, confining myself, however, solely to the elements of the even series, thus:—

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ag	Cd	In	Sn	Sb	Te	I	Xe
Au	Hg	Tl	Pb	Bi	—	—	—

Suppose, now, I wish to investigate the affinities which a given element A exhibits towards these various elements. I first of all undertake a study of the relative stability of the compounds which A produces with each of the elements of the above table, especially as egards the magnitude of the heat of formation, stability owards temperature, power of being reduced, &c.; from

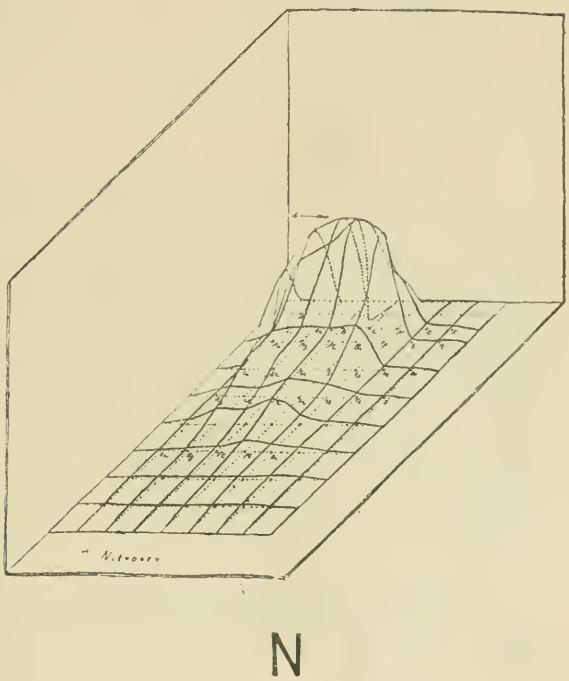


Fig. 1.—Affinity Surface for Nitrogen.

Showing at a glance how the Affinities of Nitrogen for the various Elements of the Periodic System vary. (Taken from the writer's book, "Researches on the Affinities of the Elements").

such a comparative study it is possible to arrive at a very good idea of the relative strengths of the attractive forces which the element A exerts on each of the above elements.

Next from *each* of the elements of the above table I erect a perpendicular *proportional* to the chemical attraction or affinity which it possesses for the given element A.

A surface is then described through the summits of these perpendiculars, and we get what I call the "affinity surface" of the element A, in respect to the other elements of the periodic system.

The shape of this surface shows at a glance the relative magnitude of the affinities exerted on the different elements of the periodic system.

The details of constructing these surfaces, together with all the data on which the results are founded, is collected together in the writer's book, "Researches on the Affinities of the Elements," and I do not propose to go further into

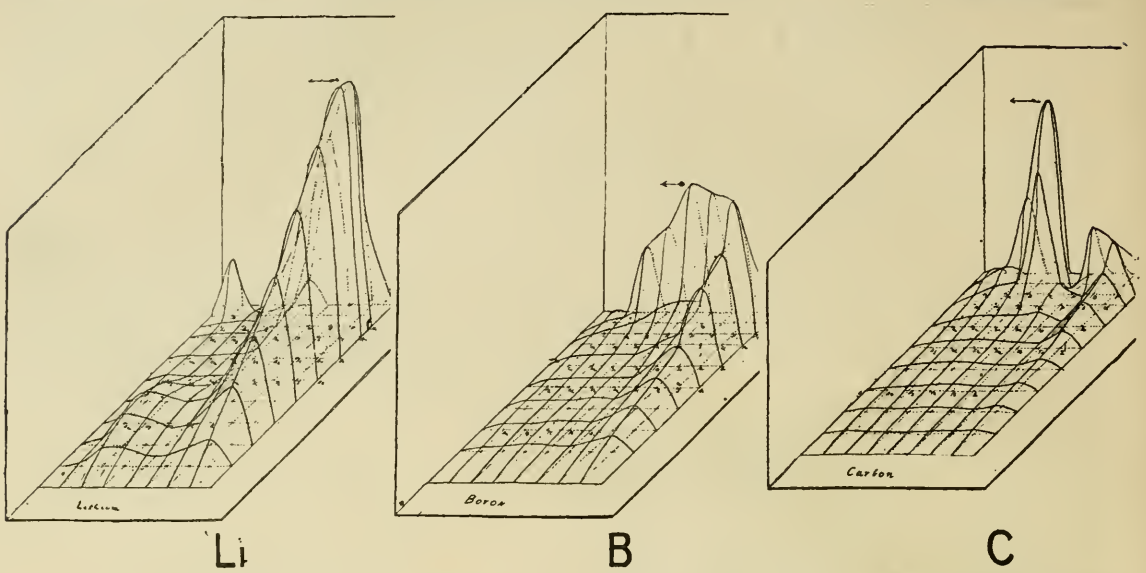


FIG. 2.—Showing how the Affinities of the successive Elements vary as we pass from Lithium

this matter here, because a detailed study of the individual compounds formed by each of the thirty-seven elements of the above table with the other elements requires a very large space for discussion, and indeed a volume of some hundreds of pages was necessary for the purpose. As this data is collected together in the above-mentioned book, I will here only apply the results obtained from a study of the affinity surfaces of the successive elements of the first two cycles of the periodic system to nitrogen so as to show that we should expect nitrogen to exhibit very strong affinities for some elements and weak ones for other elements, just as the other elements of the periodic system do.

Fig. 1 shows the form that the affinity surface assumes for nitrogen.

Description of the Affinity Surface for Nitrogen.

The numbers given refer to the heights of the perpendiculars erected from the various elements below mentioned as proportional to the affinity that nitrogen possesses for them.

Cross Sections.

Li, Be, B, C, N, O, F.—The affinity for nitrogen rises from Li to B, then falls, attaining a minimum at C, rises again at N, and then falls, becoming very small at F.

Li 4·1, Be 5, B 8, C 0·5, N 4, O 0·2, F 0·1.

Na, Mg, Al, Si, P, S, Cl.—The affinity for N is very small at Na, rises steadily, attaining a maximum at P, then falls again, becoming very small at Cl.

Na 1, Mg 6, Al 7, Si 9, P 11, S 0·2, Cl 0·1.

Cu, Zn, Ga, Ge, As, Se, Br.—The attraction is very small for Cu, rising as we pass from Cu to Zn, and it remains appreciable until As is reached, then falling it becomes very small for Se, and still smaller for Br.

Cu 0·4, Zn 3, Ga 3, Ge 3, As 3, Se 0·2, Br 0·1.

Ag, Cd, In, Sn, Sb, Te, I.—The affinity is small for Ag and Cd. It is unknown for In, Sn, Sb, but probably rises from Ag to Sb; for Sb it is very small, and is still smaller for I.

Ag 0·3, Cd 2·5, In 2·5, Sn 2·5, Sb 1·0, Te 0·2, I 0·15.

Au, Hg, Tl, Pb, Bi.—The attraction for nitrogen is very small for these elements.

Au 0·1, Hg 0·2, Tl 0·2, Pb 0·2, Bi 0·2.

Longitudinal Sections.

H, Li, Na, Cl, Au.—The attraction for N increases from H to Li and then steadily decreases until Au is reached.

H 1, Li 4·1, Na 1·0, Cu 0·4, Ag 0·3, Au 0·2.

Be, Mg, Zn, Cd, Hg.—The attraction for N in the case of Be is unknown, but probably it is greater than in the case of Mg; the affinity probably reaches a maximum in the case of Mg and then sinks, becoming very small for Hg.

Be 7, Mg 6, Zn 3, Cd 5·5, Tl 0·2.

B, Al, Ga, In, Tl.—The attraction for N at B is very great, and sinks thence to Al; the affinity of N for the other elements is unknown, but probably sinks steadily from B to Tl.

B 8, Al 7, Ga 3, In 2·5, Tl 0·2.

C, Si, Ge, Sn, Pb.—The affinity for N is very feeble at C, but it rises greatly as we pass from C to N; for the other elements it is unknown, but probably sinks rapidly from C to Pb.

C 0·5, Si 9·0, Ge 3·0, Sn 2·5, Pb 0·2.

N, P, As, Sb, Bi.—The attraction for N rises rapidly from N to P; the attraction for N of the other elements is unknown, but probably is feeble, falling from As to Bi.

N 4, P 8, As 3, Sb 1, Bi 0·5.

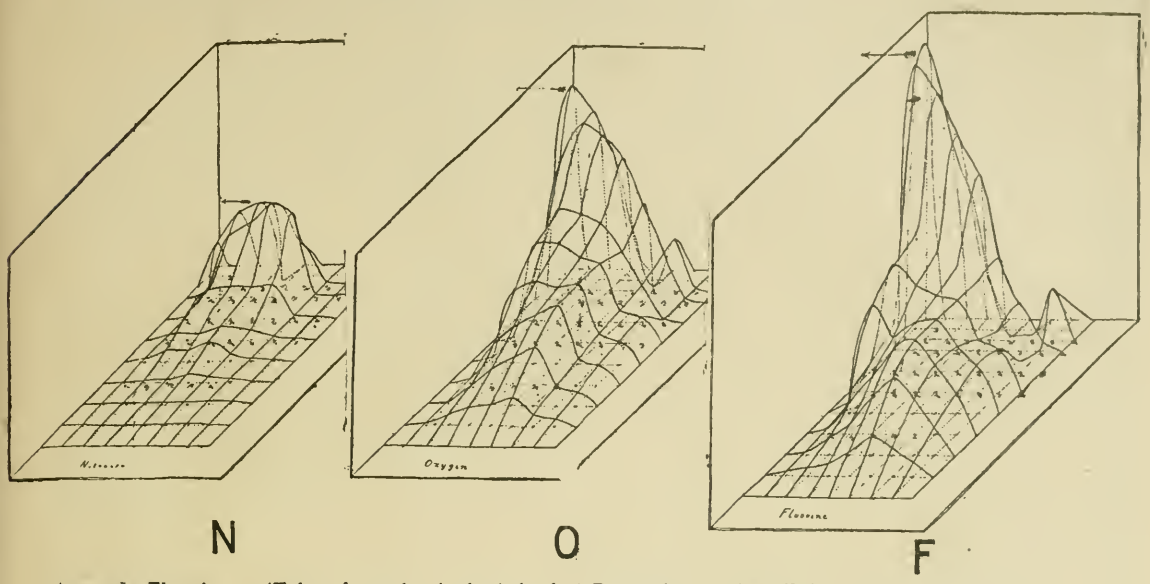
O, S, Se, Te.—The affinity for N is small all through the series, sinking from O to S, remaining about the same for Se as for S, then rising somewhat for Te.

O 0·2, S 0·2, Se 0·2, Te 0·3.

F, Cl, Br, I.—The attraction for N is very small for all these elements, being greatest for I and least for F.

F 0·1, Cl 0·1, Br 0·1, I 0·15.

Now let us compare these affinities of nitrogen with those of neighbouring elements. If we arrange in order the affinity surfaces of the first series of elements of the periodic system (viz., Li, Be, B, C, N, O, F), a remarkable fact becomes apparent, which is illustrated in Fig. 2. The affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave, whose crest appears on the extreme right hand side of the diagram in the case of Li, and then sweeps from right to left as we pass from Li towards F, until at F the crest is on the extreme left-hand side (see Fig. 2).



towards Fluorine. (Taken from the Author's book, "Researches on the Affinities of the Elements").

The same phenomenon appears with the elements of the second (Na, Mg, Al, Si, P, S, Cl, Ar) cycle, and later cycles of the periodic law, only in most cases the wave form seems to pass more or less discontinuously from right left, and *there often seems to be a depression at the elements of the fourth group, probably an apparent effect due to the abnormally developed power of self-combination possessed by these elements.* For example, when we come to compare the heats of formation of the two oxides of carbon, we have, according to Thomsen, the following numbers :—

(C, O) = 29,000 cal.,
(CO, O) = 67,960 cal.,

so that the addition of the second atom of oxygen to the carbon atom is attended with the liberation of a far greater quantity of visible heat than the addition of the first atom. This is a remarkable result, quite at variance with the usual rule (see "Affinities of the Elements," p. 241 *et seq.*) which holds in chemistry, and the explanation is, probably, that the small quantity of heat evolved in the formation of CO is due to the fact that before an oxygen atom can combine at all with a carbon atom it has to separate it from its combinations with other carbon atoms. The carbon atoms attract each other very strongly indeed, as is shown not only by their great power of self-combination, but also by the great hardness and involatility of certain forms of carbon. Consequently this initial separation of the carbon atoms absorbs a very large quantity of heat, and this lowers the apparent heat of formation of CO to much below its real value.

In gaseous CO, however, the carbon atoms are already separated, and so no further great quantity of heat is absorbed before the additional O can be added on to form CO_2. It is very probable, therefore, that the apparent heats of formation and stability of the oxides, and indeed of all other compounds of carbon, are very much below their real values on account of the exceptionally large quantities of heat absorbed in separating the carbon atoms from each other. This is probably the reason why the heat of formation of CH_4 is less than the heat of formation of SiH_4, although CH_4 is a much more stable body than SiH_4.

Silicon is the element next to carbon which possesses to the greatest extent the power of self-combination. The apparent heat of formation of its oxide is also, therefore, probably much less than its true value. In the case of certain monatomic atoms, such as those of sodium, mercury, &c., and of elements in which the power of self-combination is but slightly developed, the apparent heats of formation probably correspond fairly closely with the real heats of formation.

We should therefore expect that when we come to compare the thermal data and stability of the compounds of the various elements we will find that *there is an apparent general depression very much below their true values as we approach such elements as carbon and silicon which lie in the middle of a cycle of elements of the periodic system where the power of self-combination is largely developed ;* whereas there should be nearly correct values for such elements as Na, Hg, &c., which lie on the extreme borders of the cycle of elements, and where the power of self-combination is but feebly developed. A glance of the relative magnitudes of the affinity surfaces of the successive elements exhibited in Fig. 2 shows that this is actually the case.

Applying these results to the affinity surface of nitrogen we will now show that *the chemical inactivity of nitrogen is to a great extent only an apparent effect.*

A study of the affinity surface for nitrogen shows that the point of maximum chemical affinity lies over boron.

When we contrast the nitrogen affinity surface with those of Na or Cl, it becomes manifest that while Na expends its energies upon elements belonging to the later groups of the periodic system (viz., O, S, Se, F, Cl, Br, I), and has little affinity for elements of the earlier groups (such as the alkali metals and alkali earth metals), and that while chlorine expends its energies principally upon the elements of the early groups of the periodic system (such as the alkali metals and alkaline earth metals), but has little affinity for elements of later groups (such as the halogens and oxygen group of elements) that, in contradistinction to these, *nitrogen expends its energies on elements of intermediate groups—principally on those of Groups* III., IV., *and* V.—*but has little affinity for those of earlier or later groups* (*such as the alkali elements and the halogens*). For example, its combinations with boron, silicon, and phosphorus are quite remarkable by reason of their great stability. The phosphide P_3N_2 must be heated in oxygen gas to a temperature above that at

which hard glass melts, before the oxygen begins to act on it! When we consider the great attraction that phosphorus has for oxygen, this shows that the affinities that nitrogen exerts on phosphorus are very great.

The chemical affinities of oxygen and potassium are more apparent to us than are the chemical affinities of nitrogen, principally because they happen to possess very powerful affinities for some of the most prominent and abundant elements by which we are surrounded, whereas nitrogen possesses but feeble affinities for such elements but strong affinities for elements which happen not to be prominent or abundant in the laboratory. Nitrogen is doubly unfortunate in this respect, for *the elements for which it possesses the strongest affinity are elements which occur in the middle of cycles of the periodic system, and so are precisely those which happen to possess the power of self-combination most highly developed. This circumstance lowers the apparent stability of the compounds they produce with nitrogen in the way previously explained.*

It should be remembered that oxygen itself has only a feeble affinity for N, F, Cl, Br, I., &c., and were these the only common or prominent elements, we would consider O to be quite as inactive an element chemically as N appears to us under ordinary circumstances.

The compounds of O with Cl, for example, are characterised by their explosive properties, just as are so many nitrogen compounds.

Moreover, the nitrogen atoms themselves have a very considerable power of self-attraction, as is shown by the stability of the molecule N_2 in gaseous nitrogen, and by the occurrence of the diazo group —N = N— in organic chemistry, and this circumstance again lowers the apparent affinities of nitrogen for other elements in the way previously explained at length, for this attraction of nitrogen for itself has to be overcome before nitrogen will enter into combination with other elements.

On all these grounds, therefore, we must come to the conclusion that the current belief that nitrogen is an element characterised by its chemical inertness, and by the feebleness of its chemical affinities, is therefore hardly correct. *Nitrogen possesses chemical affinities of a strength almost comparable with those of chlorine or sodium, only it differs from these elements as regards the elements it exerts on them.*

ON SOME NEW RELATIONS OF ATOMIC WEIGHTS, AND TRANSFORMATIONS OF NEON AND HELIUM.

By Dr. HENRY WILDE, F.R.S.

At an extraordinary general meeting of the Manchester Literary and Philosophical Society, held on July 22nd, a paper was read by Dr. Henry Wilde, F.R.S., on "Some New Multiple Relations of the Atomic Weights of Elementary Substances, and on the Classification and Transformations of Neon and Helium." In several of the author's papers on the "Origin of Elementary Substances," published by the Society, 1878—1906 (see CHEMICAL NEWS, 1878, xxxviii., p. 66 *et seq.*), special attention was directed to the seventh series of his classification, on account of the magnitude and importance of its primary members in the economy of nature, viz., nitrogen, silicon, iron, and gold.

Silicon in combination with oxygen constitutes more than half the weight of the earth's crust, and is the principal constituent of glass for all the purposes of civilised life.

The arbitrary policy of several writers in doubling the atomic weights of four of the gaseous members of this series, viz., neon, argon, krypton, and xenon, induced the author to review the multiple relations of the seventh series with the important result (1) that six triads are formed out of the eight principal members of the series, in which the sum of the atomic weights of the extreme members is double the atomic weight of the means, and are all multiples of seven. Triads of atomic weights have been fully recognised by Dumas, Faraday, and other philosophical chemists, as indubitable evidence of community of origin, of transmutation, and important factors in the classification of elementary substances.

Radium (as was indicated in Dr. Wilde's tables of elements some years previous to its discovery) is one of the synthetic transformations of helium, and is the next higher member of the series of barium, as was since confirmed by Mme. Curie. Helium is also shown in the author's table of 1878, as the analytic transformation ultimate of radium and other members of the second series of elements.

The positions of helium and neon, as the transformation ultimates of the second and seventh series respectively, are further interesting in connection with the recent announcements that these elements have been found in glass vessels and tubes in which they had no previous existence. Assuming the reality of these observations, the phenomena not only admit of explication from Dr. Wilde's classifications, but also account for the discordant results obtained by the experimenters engaged in the research. One of the investigators could only find neon, while others, working independently, found helium alone, and in other cases a mixture of both gases. These results were of sufficient interest to induce the author to ascertain the composition of various glasses used in the arts.

The principal and most important constituent of the glasses tabulated by Dr. Wilde is silicon, the transformation ultimate of which is neon. The next important constituents of the glasses are barium, calcium, and lead; all members of the second series of elements, the transformation ultimate of which is helium. The alkali metals, sodium and potassium, are constituents of nearly all glasses, and their transformation ultimates (with others of the first series) will be hydrogen and neon, but without helium.

All the silicates of the first and second, and some of other series, are easily vitrified in small quantities in laboratory crucibles. Their spectra can then be examined during electrification in tubes (under suitable conditions of temperature and pressure) for the discovery of new elements, and the identification of those already known.

ANALYSIS OF FERRO-TITANIUM.

By A. R. SCOTT.

The following method for the determination of silicon, titanium, aluminium, iron, and manganese will be found very simple and accurate, especially so with regard to the complete separation of titanium and aluminium.

The method of estimating the aluminium by the long fusion with sodium carbonate, &c., is a long and tedious process, and the results obtained are not at all reliable.

Method.—Weigh out 0·25 grm. of the finely powdered alloy, and fuse with about 10 grms. of potassium bisulphate in a deep platinum basin. Fuse until no grit can be felt with a platinum rod. Cool, and put basin and contents into a porcelain evaporating basin. Extract with water, and add 10 cc. of concentrated H_2SO_4. Allow to stand on edge of hot plate for an hour. Filter into 600 cc. beaker. Wash with hot water, and ignite residue in platinum crucible. Fuse contents of crucible with a little potassium bisulphate, and extract as before with water and a few drops of H_2SO_4. Filter, and add filtrate to main filtrate. Ignite residue in a tared platinum crucible, cool and weigh. The increase in weight is SiO_2, with a little Fe_2O_3 and TiO_2. H.F. the residue, and weigh; the loss is SiO_2—calculate to silicon. Dissolve the residue in a little HCl; transfer to small beaker. Add NH_4OH, boil and filter; ignite in platinum crucible and weigh as

Fe_2O_3. Calculate to Fe. Any difference in the weight of residue after volatilisation of SiO_2 will be TiO_2; calculate to Ti.

Titanium.—Boil up combined filtrates from the SiO_2, and add ammonium hydrate until slight precipitate appears; clear with a few drops of hydrochloric acid, and add about 15 grms. sodium thiosulphate dissolved in water. Boil for fifteen minutes, and filter through pulp filter. Wash with acetic water. Transfer precipitate to tared platinum crucible, ignite strongly, and weigh as TiO_2. Calculate to Ti.

Iron and Aluminium.—Boil down the filtrate to fairly low bulk, and add about 200 cc. of hot water; boil down again. Continue the addition of water and the boiling until clear. Oxidise with bromine water, filter off any TiO_2 that may have got through the filter, and ignite same. Boil up the filtrate and add ammonium hydrate; filter into conical flask. Ignite the precipitate, and weigh as $Fe_2O_3+Al_2O_3$. Dissolve up the combined oxides in hydrochloric acid, reduce with stannous chloride, and titrate the Fe with potassium dichromate in the usual way. The difference after calculation will be *aluminium*.

Manganese.—To the cooled filtrate add bromine and ammonium hydrate, boil and filter. Ignite, and weigh as Mn_3O_4. Calculate to Mn.

Old Hall Road, Galley.

PREPARATION OF THE NITRITES OF THE PRIMARY, SECONDARY, AND TERTIARY AMINES BY THE INTERACTION OF THE HYDROCHLORIDES OF THE BASES AND ALKALI NITRITES.

Explanation of the Action of Nitrous Acid on the Amines.

(Part I.).

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry, Government College, Rajshahi, Bengal, India.

Neogi and Adhicari (*Trans. Chem. Soc.*, 1911, xcix., 116) have already shown that ammonium nitrite can be prepared in fairly large quantities by subliming in a vacuum a concentrated solution of the mixture of ammonium chloride and alkali nitrites. Neogi (*Trans. Chem. Soc.*, 1912, ci., 1608) has also shown that coniinium nitrite may be prepared by distilling in a current of steam under reduced pressure a mixture of the hydrochloride and sodium or potassium nitrites. In continuation of the work referred to above, a systematic attempt has been made to prepare the amine nitrites by the interaction of the hydrochlorides of the bases and alkali nitrites. Experiments have abundantly shown that this method of preparing the amine nitrites is a general one. The success of the isolation of the amine nitrites from mixtures of the hydrochlorides of the bases and alkali nitrites lies on two facts hitherto unobserved :—

1. The amine nitrites may be distilled off in steam under reduced pressure in a very pure condition.

2. The amine nitrites, which are comparatively unstable in the solid or liquid condition as the case may be, are, in general, *stable in solution*, and, in fact, most of them may be concentrated to a small bulk on the water-bath without great loss.

The actual isolation of ammonium nitrite and a large number of amine nitrites affords ample confirmation of the theory already advanced by the author (Neogi, *Proc. Chem. Soc.*, 1911, xxvii., 242; *Trans. Chem. Soc.*, 1912, ci., 1610), that an amine nitrite is an intermediate compound in the well known interaction of amine hydrochlorides and sodium or potassium nitrite, or, in other words, amines and nitrous acid. The following equations show how the reactions really take place in two stages :—

(*a*) Ammonia or primary amine,—

$$R.NH_2+HNO_2=R.NH_2.HNO_2=R.OH+N_2+H_2O.$$

(*b*) Secondary amine,—

$$R_2NH+HNO_2=R_2NH.HNO_2=R_2N.NO+H_2O.$$

(*c*) Tertiary amine :—

$$1.\ R_3N+HNO_2 \rightleftharpoons R_3N.HNO_2.$$

$$2.\ 3R_3N.HNO_2=2R_3N+R_3NO_3+2NO+H_2O.$$

The nitrite is formed in each case at a low temperature, which decomposes at a higher temperature into the end-products of the respective reactions, viz., alcohol and nitrogen in the case of primary amines, nitroso-compound in the case of secondary amines, and the free amine in the case of the tertiary amines. In the case of the tertiary amines, however, the corresponding nitrates are also formed as a result of the decomposition of the nitrites.

This explanation does not, as a matter of course, apply to the purely aromatic amines which yield diazo-compounds.

Experimental.

The hydrochlorides of the amines were mostly indented from Kahlbaum, a few being obtained from E. Merck. They were found to be very pure, and were further purified from traces of ammonium chloride by exhausting them with small quantities of dry absolute alcohol, in which they were found to be almost wholly soluble. The general method of preparing the amine nitrites consists in vacuum distillation in steam. In the case of those nitrites, however, which sublime when heated in a vacuum, attempts were also made to isolate them by vacuum sublimation.

Sublimation in Vacuum.

One or 2 grms. of the hydrochloride were mixed with excess of sodium or potassium nitrite, and dissolved in a very small quantity (10 to 20 cc.) of water. The liquid was evaporated in a flask with a long neck, provided with a "catch" arrangement in order to avoid spirting, at 40° to 50° in the vacuum of the Töppler pump, and the gases evolved were collected in a Crum nitrometer. In order to drive off the last traces of moisture the entire neck of the flask was immersed in the bath. A capacious test-tube immersed in a beaker of cold water was inserted between the flask and the pump, which served as a condenser. The flask was held in a very slanting position so that particles of the liquid might not spirt into the neck of the flask. After the liquid was completely evaporated to dryness and traces of moisture had been driven off, the neck of the flask was partially raised, and the temperature of the bath was also gradually raised to the temperature at which the nitrite sublimed. When the experiment was completed the bottom of the flask was broken off, and the sublimed salt carefully washed out with water, mixed with the distillate contained in the test-tube, and the solution thus obtained was evaporated in a vacuum desiccator. The crystals were analysed by the "urea" and Crum-Frankland methods. As only small quantities of the hydrochloride were available the yield was not very satisfactory by this method. The success of the experiment will depend on the success with which the last traces of moisture have been driven off from the flask, as the nitrites are extremely hygroscopic.

Vacuum Sublimation in Steam.

A much better yield, however, of the nitrite was obtained by the process of vacuum distillation in steam. The operation was conducted in two ways:—(1) Distilling the solution in a current of steam whilst a vacuum was maintained, and (2) repeatedly distilling in a vacuum the mixture with fresh quantities of water. The first of these two processes has the advantage of being continuous, but the bumping is severe. The second process gives the better yield. The best results were obtained in the following manner :—The solution of the mixture was placed in a

distilling flask not less than 1 litre in capacity connected with a long condenser and receiver, which was in turn connected with a Geryk pump and manometer. The solution was diluted with water so as to fill not more than one-third of the flask, which was held in a very slanting position in order that the liquid might not spit into the neck of the flask. The flask was immersed in a capacious beaker containing water, which served as a bath. The distillation was conducted at a temperature suited to each case until the volume of the liquid was reduced to 30 to 50 cc. The flask was then thoroughly cooled, and the receiver detached. More water was added to the flask and a second distillate obtained. In this way several distillates were collected so long as they contained appreciable quantities of the nitrite. The total volume of the distillates with 1 or 2 grms. of the hydrochloride was between 300 to 500 cc. The nitrite, except in the case of ammonium nitrite, was wholly free from chloride. In this way 60 to 80 per cent and in some cases almost theoretical quantity of the nitrites, passed into the distillate, provided the temperature at which distillation was conducted was sufficiently low and the volume of the distillate sufficiently large.

In order to obtain the solid or liquid nitrite from the large volume of the distillate two methods were employed. In the case of those nitrites the solutions of which decompose to a large extent when heated on the water-bath, 100 cc. of the distillate was divided into four portions, each portion being kept in a vacuum desiccator. As the liquid in each diminished in quantity the four portions were mixed together and finally crystallised in one desiccator. In this way a good yield of the solid or liquid nitrite was obtained in three or four days. In the case of those nitrites the solutions of which do not decompose to a large extent when concentrated to a small bulk on the water-bath, the distillate was evaporated to a small bulk on the water-bath, and finally crystallised in a vacuum desiccator. Experiments show that the solutions of the great majority of the amine nitrites are fairly stable, and that they may be concentrated on the water-bath to a small bulk without great loss either by decomposition or volatilisation with steam at atmospheric pressure. The nitrites, as usual, were estimated by the "urea" and Crum-Frankland methods. Below are given results with each hydrochloride and sodium or potassium nitrite.

Interaction between Ammonium Chloride and Sodium or Potassium Nitrite. Steam Distillation in Vacuum.

Neogi and Adhicary (*Trans. Chem. Soc.*, 1911, xcix., 116) have already shown that pure ammonium nitrite may be prepared by first concentrating at about 50—60°, and then *subliming* at 80° a strong solution of this mixture.

It has been shown here that it can be prepared by steam distillation in vacuum also. The process as well as the apparatus employed have already been described before. One to 5 grms. of ammonium chloride were taken and mixed with excess of sodium or potassium nitrite. If the quantity of the distillate is large enough, almost quantitative yield of ammonium nitrite passes into the distillate, as will be seen from the following table. The temperature of the bath was maintained at 70°.

Wt. of NH_4Cl.		Vol. of distillate. Cc.	Wt. of $NH_4.NO_2$. Grms.
1 grm.	1st	210	0·63
	2nd . ..	140	0·32
	3rd	165	0·02
5 grms.	1st	122	1·00
	2nd . ..	106	0·77
	3rd	245	1·50
	4th	220	1·01
	5th	132	0·11

There was no nitrate in the distillate, as the "urea" nitrogen was equal to the nitric oxide by the Crum-Frankland method. Slight turbidity was produced by the addition of silver nitrate, thus showing that minute quantities of ammonium chloride pass into the distillate. The solid nitrite was obtained by concentrating 100 cc. of the first distillate in four vacuum desiccators, and freed from any ammonium chloride by means of absolute alcohol, in which it was almost wholly soluble. The operation took four days. The salt was white, slightly tinged greenish, extremely deliquescent, and very soluble in water and alcohol.

0·1160 gave 48·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc. with water, of which 1 cc. = 4·8 cc. N_2), hence N ("nitritic") = 22·2 per cent. $NH_4.NO_2$ requires N (nitritic) = 21·8 per cent.

Attempts were also made to obtain the solid nitrite after concentrating the dilute distillate to a small bulk on the water-bath. 250 cc. of the distillate containing 1·36 grms. ammonium nitrite was concentrated on the water bath to 20 cc. It was found that the concentrated liquid still contained 54·3 per cent ammonium nitrite, the rest either decomposing into nitrogen and water or passing away with steam. The proportion of ammonium nitrate was small, as the ratio of the volumes of nitrogen and nitric oxide was 11·4 cc. + 11·8 cc. The crystals obtained in this way were more greenish in appearance and contained appreciable quantities of this nitrate. Thus this process might serve as a rapid method of obtaining not very pure samples of ammonium nitrite, the pure substance being obtained by crystallising without concentration on the water-bath.

As ammonium nitrite decomposes according to the equation $NH_4NO_2 = N_2 + 2H_2O$, the evolution of nitrogen by the action of ammonium chloride and sodium or potassium nitrite, or, in other words, of nitrous acid on ammonia, is simply the end-product of the reaction, the intermediate compound being ammonium nitrite.

The general similarity of the properties of ammonia and the primary amines, and particularly the similarity in the action of nitrous acid on ammonia and the primary amines, induces the author to regard ammonia as a primary amine. The name hydramine is suggested for ammonia, regarding it as a primary amine.

Benzylammonium Hydrochloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

One or 2 grms. of the hydrochloride purified from absolute alcohol (Cl = 23·8 per cent found, Cl = 24·7 per cent calc.) were taken, and the mixture of the hydrochloride and alkali nitrite was dissolved in a minimum quantity of water and transferred to the flask, and the Töppler set to work. The temperature of the bath was maintained between 40° and 50° during the evaporation of the water. Only very small quantities of nitrogen collected in the nitrometer, thus showing that very little action took place in solution. The entire neck of the flask was immersed in the bath, and when no more water remained in the flask, it was partially raised, and the temperature raised to 60°, when white crystals began to collect in the cooler parts of the neck of the flask, and at 60° to 70° a good quantity collected in white clusters of crystals. A small quantity of a gas collected in the nitrometer in the meantime, which was found to be nitrogen. On disconnecting the apparatus the sublimed salt was found to be pure benzylammonium nitrite containing no chloride. Blank experiments showed that in vacuum benzylammonium hydrochloride commenced to sublime at about 130°. The distillate contained in the test-tube also contained appreciable quantities of the nitrites free from chloride. The two solutions were mixed together, crystallised in a vacuum desiccator, and tested. The crystals were white, deliquescent, very soluble in water and alcohol.

If, however, the temperature was rapidly raised to 80° and above, the salt began to melt, and finally disappeared, and at the same time the evolution of gas was brisk. The gas on examination was found to be almost pure nitrogen, and the liquid in the test-tube an aqueous solution of benzyl alcohol, which was recognised by its smell and conversion into benzaldehyde on oxidation with nitric acid. The formation of benzyl alcohol and nitrogen is very

readily explained as the result of the decomposition of benzylammonium nitrite according to the equation (*cf.* Ray and Datta, *Trans. Chem. Soc.*, 1911, xcix., 1476)

$$C_6H_5.CH_2.NH_2.HNO_2 = C_6H_5.CH_2.OH + N_2 + H_2O.$$

(To be continued).

THE SULPHOCYANATE-PERMANGANATE METHOD FOR COPPER IN ORES.

By D. J. DEMOREST.

UNDER the proper conditions copper may be precipitated practically completely as cuprous sulphocyanate. It is true that a qualitative test for copper may be obtained in the filtrate from the cuprous sulphocyanate when potassium ferrocyanide is added, but this is due to the presence of only about 0·0001 grm. of copper, as the writer has found by colorimetric measurements. Furthermore, the writer has found that practically all the copper added to the solution before precipitation may be recovered from the precipitate by electrolysis.

In Guess's method for copper the cuprous sulphocyanate is dissolved on the filter with sodium hydroxide, leaving the cuprous hydroxide on the filter while sodium sulphocyanate goes through. The filtrate is then made acid with sulphuric acid and is titrated with permanganate. Theoretically, the titration reaction is—

$$5HCNS + 6KMnO_4 + 4H_2SO_4 = 5HCN + 3K_2SO_4 + 6MnSO_4 + 4H_2O.$$

Practically, however, the oxidation in acid solution is never complete, and an empirical factor must be used amounting to about 5 per cent of the copper present, according to Guess's tables of correction given in Low's "Technical Methods of Ore Analysis." This is also in accord with the writer's experience and with that of Grossman and Hölter (Grossman and Hölter, *Chem. Ztg.*, xxxiii., 348).

It occurred to the writer that if the permanganate were added to the sulphocyanate in alkaline solution until about as much was added as would be required to titrate the sulphocyanate in acid solution, and if then the solution were made acid, the titration might be finished by a few drops, and in this way complete oxidation might be brought about and no empirical factor would be needed.

It is easy to tell when enough permanganate has been added to the alkaline solution by testing a drop or so on a white plate with a drop of an acid solution of ferric chloride. If not enough permanganate has been added a red colour develops, but if enough has been added no red appears. It is not necessary to run in permanganate until no red is obtained on testing. When the red colour of the test is very faint the solution may be made acid and the titration finished in the usual way.

Process of Analysis.

Weigh out enough of the ore to have from 0·05 grm. to 0·30 grm. of copper present. Transfer the sample to a 200 cc. beaker, add 5 cc. of strong hydrochloric acid and heat for several minutes; then add 10 cc. of nitric acid and digest on a hot plate until the oil is completely decomposed. Then add 10 cc. 1 : 1 sulphuric acid and boil down until fumes of SO_2 appear. Cool and add 50 cc. of water containing 3 grms. of tartaric acid and heat until all soluble salts are in solution. Cool and add ammonia until the solution turns a deep blue, then add sulphuric acid until the liquid becomes acid, then add 1 cc. more. Now add 1 grm. of sodium sulphite dissolved in 20 cc. of water, heat nearly to boiling, and add slowly and with vigorous stirring 1 grm. of potassium sulphocyanate dissolved in 20 cc. of water. Heat at a nearly boiling temperature for several minutes to coagulate the precipitate and dissolve out of it all tartaric acid. Cool somewhat and filter while still hot through, preferably, an asbestos mat on a Gooch filter. Wash well with water and rinse out the suction flask. Then pour through the crucible 30 cc. of a hot 10 per cent sodium hydroxide solution and wash well with water.

Warm the filtrate to about 50° and proceed to titrate. Run in slowly at first, while the flask is vigorously shaken, the standard permanganate solution. The solution in the flask turns green, due to the K_2MnO_4 formed. After about 10 cc. have been run in, take out a drop of the solution and place it in a drop of strong hydrochloric acid on a paraffined white plate; then add a drop of a 10 per cent solution of ferric chloride. If a red colour appears continue to add the permanganate solution, testing after each 5 cc. until the red becomes weak, then test more frequently until the red colour of a test becomes quite faint. Then add 30 cc. of 1 : 1 sulphuric acid and shake the flask until the MnO_2 all dissolves and finish the titration to the usual permanganate end point. This will require perhaps 1 cc. of permanganate.

Notes on the Process.

Fairly close results may be obtained by titrating carefully in the alkaline solution until five drops of the solution give no red colour with ferric chloride. But it is easier and more accurate to titrate only to an approximate end in the alkaline solution and finish in an acid solution. It is important that the precipitation be made as above directed with vigorous stirring and that the solution be digested on the hot plate after precipitation.

Under the conditions of titration the permanganate is reduced in the alkaline solution thus:—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + 2O.$$

The oxygen possibly oxidises the sulphocyanate to tetrathionate, but of this the writer is not sure. He has proved by filtering off the MnO_2 and weighing it and by titrating the permanganate in the filtrate that the permanganate is reduced as above written. However, it makes no difference what reaction takes place in the oxidation of the sulphur in the alkaline solution, since the test for sulphocyanic acid is made on the plate in a strongly acid solution and the reaction between the sulphocyanate and the manganate and manganese dioxide completes itself there. The manganese dioxide does not settle out of the solution unless it stands a long time.

According to the titration reaction given in the second paragraph of this article 5 atoms of copper are equivalent to 6 molecules of $KMnO_4$ or 30 atoms of iron. Therefore, the iron value of the permanganate multiplied by Cu/6Fe or 0·1897 gives the copper value of the permanganate. The permanganate used by the writer equals 0·01 grm. Fe, or 0·001897 grm. Cu per cc.

After the filtrate has cooled, a crystalline compound of tartaric acid may separate. Hence the solution should be filtered hot.

The following are some results obtained by the above method :—

Copper.		Copper.	
Present.	Found.	Present.	Found.
0·1870	0·1890	0·0600	0·0596
0·1503	0·1511	0·0605	0·0603
0·1117	0·1125	0·1610	0·1630
0·1666	0·1668	0·0663	0·0667
0·0940	0·0930	0·1103	0·1109
0·2005	0·2017	0·1140	0·1147
0·2220	0·2224	0·1000	0·1001
0·2220	0·2210	0·1000	0·0999

The later results were the most accurate and were obtained after the necessity of digesting the precipitate in the hot solution was learned.

No elements interfere except, according to Low, silver. This is easily removed. If there is any lead present, the lead sulphate obtained after evaporating to fumes of SO_3 should be filtered off after the soluble salts are dissolved. —*Journal of Industrial and Engineering Chemistry*, v., No. 3.

REPORT ON THE ACTUAL STATE OF RUBBER ANALYSIS.*

By Prof. F. WILLY HINRICHSEN, Berlin.

In view of the great difficulties which the analyses of crude and of vulcanised rubber offer we should endeavour to agree upon the various methods of analysis, in order that similar tests conducted at different spots will lead to the same results. An international agreement upon this question would be particularly desirable.

I. *Analysis of Crude Rubber.*

The crude rubber contains, as is well known, in addition to the caoutchouc proper and to the mechanical impurities, such as sand, bark, &c., also moisture, mineral constituents, resins, and albuminoids. Of practical importance are above all the contents in pure rubber or caoutchouc, in mechanical admixtures, and in resins. The percentage of the latter affords a certain measure for the technical value of a kind of rubber, since the product is considered all the more valuable, the smaller its percentage in resins. The mechanical impurities are removed in the works by washing with water between rollers. The magnitude of the loss by washing is a second criterion for the applicability and the value of a commercial product. This washing loss is ascertained in the laboratory in a similar manner as in the works, by washing a sample of rubber on a small experimental roller. It is primarily essential for these experiments that the sample selected represent a fair average of the product.

As regards the chemical analysis of crude rubber, we should in the first instance determine whether the test is to be made with the original material or with the washed material. It would in general appear advisable always to make use of the washed material which has been air-dried.

The moisture is suitably determined in a specially weighed portion by drying *in vacuo* over sulphuric acid at gentle heat, until the weight remain constant.

For the determination of the resins 5 grms. of the finely-cut air-dried materials are completely extracted with acetone in a Soxhlet apparatus. Ten hours will in general be sufficient for this operation; the middle portion of the Soxhlet apparatus is suitably made of brown glass in order to prevent any action of the light on the material to be extracted. The dimensions of the apparatus to be used should be agreed upon, since any deviations from these dimensions would alone affect the values found for the percentages of the resins.

The further tests of the resins for optical activity and saponification which can be made according to Hinrichsen and Marcusson, permit under certain conditions to draw conclusions as to the botanical origin of the product.

Several processes have been suggested for the direct determination of pure caoutchouc; among these are the reaction with nitrous acid leading to the production of nitrosites, and the tetrabromide reaction. The recent scientific investigation of these two methods has led to the result that both these tests are unreliable. We are hence limited, as before, to an indirect analysis. For this we require, in addition to the already mentioned determination of moisture and to the extraction with acetone, in the first instance the estimation of the percentages of mineral constituents and of albuminoids. The former can as a rule be deduced from the determination of the ashes. An approximate measure for the proportion of albuminoids present is afforded by the determination of the nitrogen percentage which is suitably effected by the method of Kjeldahl. By multiplying the resulting figure by 6·25, corresponding to a content of from 15 to 18 per cent of nitrogen in the albuminoid, the amount of albuminoids in the sample is approximately deduced. The difference between the component percentages of the impurities and 100 yields the percentage of pure caoutchouc in the material.

II. *Analysis of Vulcanised Rubber.*

The compositions of the various vulcanite rubber articles are so very manifold that a generally available method of analysis cannot be suggested. In many cases the constitution of the mixture cannot even approximately be ascertained by chemical means. When it is required to fix the conditions of supply for rubber materials, whose chemical composition is to be prescribed and to be controlled, we have for the present to bear the imperfection of our methods of rubber analysis in mind. Starting from this point of view the united German cable manufacturers have, for instance, prescribed for the standard leads a rubber mixture, which contains nothing but constituents that can be determined analytically with a certain degree of reliability, namely, in addition to rubber and to sulphur only inorganic additions and hydrocarbons of the paraffin series (ceresin).

Since the methods for the direct determination of pure caoutchouc (nitrosite, bromide, &c.) are still less applicable to vucanised products than they are to the raw material, we have to have recourse to the indirect analysis. In many cases the following mode of procedure will be satisfactory, especially when pitch, tar, asphalt, and similar materials are absent.

Five grms. of the sample are extracted with acetone in the same way as we described above for crude rubber. This process will dissolve, in addition to the resins originally present in the rubber and to any foreign resins possibly added, the free sulphur, further oils, hydrocarbons of the paraffins, and wax. The sulphur is determined in a special sample in the residue, which remains after evaporating the acetone solution, after oxidation with strong nitric acid to which a little free bromine should be added. Solid hydrocarbons are approximately estimated by taking up the residue of the acetone solution with alcohol and by precipitating from this solution the hydrocarbons by continued cooling down to $-5°$ C. When oils and foreign resins are present, an exact determination of the original rubber resin is not possible. The saponification figure does not constitute any measure for the amount of the additions, since some of the original rubber resins are themselves quite incapable of undergoing saponification, while parts of them may be highly saponifiable; it depends upon the origin of the material. When in addition to these resins only free sulphur and paraffin hydrocarbons are present, the resins may approximately be estimated by difference.

The material extracted with acetone is heated with hydrocarbons of high boiling point, for instance, petroleum or oil of paraffin, for the purpose of estimating the inorganic additions; these chemicals dissolve vulcanised rubber. The mineral additions (fillers) are, if possible, removed by filtration, if not, by centrifugation of the solutions which have been precipitated with benzine and have been washed with other organic solvents.

Another portion of the material which has been extracted with acetone is boiled for four hours under application of a reflux condenser with semi-normal alcoholic soda lye. The lye will saponify the usual technical factices. After filtering off the unchanged material, water is added to the solution; by addition of mineral acids the factice-acids are then precipitated, taken up with ether and determined. Any conclusion as to the percentage of the originally added factice is unsafe for this reason already, that the different kinds of commercial factices contain very strongly varying proportions of constituents soluble in acetone.

When we want to deduce the amount of pure caoutchouc in the mixture, we need now only proceed to the estimation of the bound sulphur. For this purpose we determine the total amount of sulphur in the mixture and we deduct from this the free sulphur, the sulphur which is inor-

* Paper presented at the Sixth Congress of the International Association for Testing Materials, New York. From *Chemical Engineer*, xvii., No. 4.

ganically bound, and the sulphur which is contained in the factice-acids.

The determination of the total sulphur is simplest and safest carried out by the other process, oxidation with nitric acid and with magnesium nitrate in a spherical flask, or by the Hinrichsen process, electrolytic oxidation in nitric acid. The sulphur which was bound by inorganic compounds is directly estimated in the filling materials, and the factice-sulphur is found in analysis of the factice-acids.

If we further know the moisture and the nitrogen (albuminoid) contents of the samples, the difference will give us approximately the percentage of pure caoutchouc.

When the mixture contains, in addition to the in gredients above specified, also tar, pitch, asphalt, or similar materials, any reliable analysis of the product may be regarded as out of question. Extraction by means of pyridin has formerly been proposed; it is inapplicable, however, since the pyridin also dissolves some rubber.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

This paper is a compilation of data collected from all the available literature and contributed to the Symposium on the Electrodeposition of Metals, in accordance with the request of the President of the Society.

Tin is largely used as a protective coating to articles of iron, steel, copper, brass, and bronze. The process of coating large articles of iron, steel, and copper by merely bringing their cleaned surfaces in contact with molten tin and then removing the excess either by means of rolls or by centrifugal machines, is so much cheaper than electrolytic methods, and moreover gives such sound and perfect coatings, that the electrodeposition methods have found little application except for coating small articles and those which have an irregular surface.

A great amount of electrodeposition of tin is done for the coating of small articles such as pins, hooks, eyes, screws, clasps, &c., for which purpose this method is preferable. Another application of electrodeposition is that of giving a preliminary coating to iron or steel, which is subsequently to receive an electrodeposit of a metal which is more electropositive than iron.

The consideration of electrolytes, as given below, was done in the following order under each of the headings:—A—Acid Electrolytes, B—Neutral Electrolytes, C—Alkaline Electrolytes.

I. *Electrodeposition of Tin by Immersion.*

The use of the immersion process of tinning is principally for coating small articles of copper, brass, and iron, such as hooks, eyes, pins, buttons, clasps, screws, &c., with a thin bright adherent deposit of tin. The immersion method consists in placing the articles in contact with either metallic tin or zinc in a boiling solution of a tin salt or a solution containing a tin salt and one or more salts.

1. One of the most generally used immersion baths is a saturated solution of cream of tartar (potassium hydrogen tartrate) to which has been added from 15 to 30 grms. of tin chloride per litre. Boil and place the articles in the boiling solution, and stir with a rod of metallic tin (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electroplating," 1912 Ed., p. 221). Instead of using a rod of tin to stir the solution the articles may be placed in alternate layers with granulated or sheet tin, which will cause the articles to be coated with a white smooth adherent deposit of tin (Fields, "Principles of Electroplating," 1912 Ed., p. 211). If the metallic tin be replaced by metallic zinc, and stannous chloride added to the solution from time to time, thicker deposits of tin on the articles may be obtained and in a shorter time. In this case no tin is being added to the solution to replace that which is deposited on the articles, so it will be necessary to reject the solution when much zinc has accumulated in it (Fields, "Principles of Electroplating," 1912 Ed., p. 211; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; "Metal Industry," 1906, iv., 225). The articles, after proper coating has been obtained, should be rinsed in water, dried by shaking with sawdust, and polished with a scratch brush or by rolling in a polishing barrel.

2. An immersion solution which has given satisfaction for coating iron and steel articles with tin was used by Roseleur. It is prepared by dissolving 20 to 30 grms. of ammonium alum and 1 to 2 grms. of anhydrous tin chloride per litre of water (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; *Brass World*, 1912, viii., 180). Potash alum does not give good results. Fused tin chloride is used because it does not contain any free acid which will cause the coating to peel. The solution must be used boiling, and the iron articles must be clean of rust and grease, which are removed by an "alkali dip" and by a pickling solution. A bright coating of tin will be produced within thirty to sixty seconds. The solution must be replenished with tin from time to time by adding fused tin chloride in the original proportion to the volume of solution. As iron stands above tin in the E.M.F. series, the iron replaces an equivalent of tin in the solution, so when iron has accumulated to an amount which causes the coating to deposit in non-adherent form the solution must be rejected.

3. The solution devised by Elsner for coating copper and brass articles, and which gives reliable results (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333) is prepared by dissolving 2 grains of sodium chloride and 2 grains of stannous chloride in 1 litre of water. It is used in the same manner as solution 1.

II. *Electrolytic Determination of Tin.*

Tin may be quantitatively precipitated from certain solutions by electrolysing them under such conditions of temperature, composition, or solution, and current density as have been found to give accurate results. The solutions which give the most satisfactory results are in most cases those which contain the tin either as ammonium sulphostannate.

1. Smith states that tin may be quantitatively deposited from a solution which contains ammonium oxalate (Smith's "Electro-analyses," 1911 Ed., p. 169; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 149). Potassium oxalate is not advisable, as a basic salt of tin is liable to separate upon the anode. The conditions which were found to give good results are:—The solution, 125 to 150 cc. in volume, containing about 0·5 grm. of tin as chloride and about 4 grms. of ammonium oxalate, is acidified with 9 to 10 grms. of oxalic acid (acetic acid may be used instead of oxalic acid), heated to about 65° C. and electrolysed at C.D. of 1 to 1·5 ampère per sq. decimetre. Deposits formed under these conditions are bright and adherent.

2. Classen found that dense bright adherent deposits could be quantitatively formed in an acid ammonium oxalate solution. He added 120 cc. of a saturated solution of ammonium oxalate to 25 cc. solution containing 0·9 to 1·0 grm. of stannic ammonium chloride, then electrolysed at 30° to 35° C. with current of 0·3 to 0·6 ampère and voltage at 2·8 to 3·8. Acid ammonium oxalate must be added at intervals if a larger quantity of tin is to be deposited. Time required was about nine hours for complete precipitation. The tin separated as a brilliant white adherent deposit. It was washed, dried, and weighed in usual way (Smith's "Electro-analysis," 1911 Ed., p. 169;

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii., No. 6.

Neumann-Kershaw, "Electric Methods of Analysis," 1898 Ed., p. 149).

In case the tin is to be determined in a solution containing it as potassium sulpho-stannate, Classen recommends that it be converted into the oxalate, and then electrolysed. This is accomplished by acidifying the solution with hydrochloric acid, then boiling off the hydrogen sulphide, and adding hydrogen peroxide to oxidise the tin to metastannic acid, which is a white precipitate. Add a few cc. of sulphuric acid, neutralise with ammonia, and again add hydrogen peroxide. Filter out the metastannic acid, wash, dissolve in a solution of oxalic acid and ammonium oxalate, and electrolyse under conditions given above. Use ordinary platinum electrodes.

3. C. Engel gave the following conditions for quantitatively depositing tin by electrolysis as a bright white smooth adherent deposit:—Add to the solution, containing about 1 grm. of tin as ammonium stannic chloride, a few cc. of oxalic acid solution to clear the turbidity, then add 0·3 to 0·5 grm. of hydroxylamine hydrochloride or sulphate, 2 grms. ammonium acetate, and 2 grms. tartaric acid. Dilute to 150 cc., heat to 60° to 70° C., and electrolyse at C.D. of 0·9 to 1 ampère per sq. dm. and potential of 4 to 5 volts (*Journ. Soc. Chem. Ind.*, xv., 219; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Smith's "Electro-analysis," 1911 Ed., p. 171).

4. Campbell and Champion determined tin in ores by fusing 1·0 grm. of the finely ground sample with 5 to 6 grms. of a mixture of equal parts of sodium hydroxide and sulphur for one and a-half hours at red-heat in a porcelain crucible. The fusion was then digested with 40 to 50 cc. of hot water, the solution filtered, and the residue washed and discarded. The filtrate was acidified with hydrochloric acid, which precipitated the tin as stannic sulphide, boiled off the hydrogen sulphide, added 10 cc. concentrated hydrochloric acid, and gradually introduced 2 to 3 grms. of sodium peroxide until a clear solution was obtained. Boiled about three minutes, then filtered out the separated sulphur and washed. Added ammonia to the filtrate to permanent precipitation, and then 50 cc. of a 10 per cent acid ammonium oxalate solution. Electrolysed over night at C.D. of 0·1 ampère per sq. dm. and about 4 volts. Deposit of light colour and very adherent (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150).

In the course of any analysis, when tin is obtained as sulphide, the electrolytic determination may be conducted by getting the precipitate into solution as chloride by digesting it at boiling with 10 cc. of concentrated hydrochloric acid and 70 cc. of water, to which is gradually added 2 to 3 grms. of sodium peroxide. Then proceed in the same manner as given above (*Journ. Soc. Chem. Ind.*, xvii., 1073).

5. Pasztor rapidly and quantitatively deposited tin from tartaric acid solutions which contained from 4 to 6 grms. of tartaric acid, 2 to 6 grms. of ammonium acetate, and 1 to 1½ grms. of hydroxylamine hydrochloride or sulphate per 150 cc. volume, electrolysed at 60° to 80° C. at C.D. of 0·8 to 1 ampère per sq. dm.

Pasztor also stated that stannous sulphide dissolved in hot hydrochloric acid solution containing ammonium chloride gave a clear solution from which the tin was quantitatively deposited (*Electrochem. Zeit.*, xvi., 281; Smith's "Electroanalysis," 1911 Ed., p. 171; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Arrhenius, "Text-book of Electro-chemistry," p. 274).

6. Classen discovered that a dilute solution of tin containing an excess of ammonium sulphide would yield a quantitative deposit of the metal, but that the deposits formed in a sodium or potassium sulphide solution were dark grey and non-adherent (Smith's "Electro-analysis," 1911 Ed., p. 170; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150). The conditions for obtaining a satisfactory deposit of tin from ammonium sulphide solution containing the tin as ammonium sulphostannate are:—150 cc. solution containing an excess of ammonium sulphide, heated at 50° to 60° C., and electrolysed at C.D. of 1 to 1½ ampère per sq. dm. and potential of 4 to 5 volts (Arrhenius, "Text-book of Electro-chemistry," p. 274).

Use of Rotating Electrodes.—The use of rotating anodes, revolved at 300 to 500 times per minute, enables the quantitative precipitation of tin to be made from ammonium oxalate solutions and ammonium sulphide solutions in twenty to thirty minutes, giving a deposit like polished silver. The electrolysis is conducted with C.D. of 5 to 8 ampères per sq. dm. and E.M.F. of 5 to 8 volts (Smith's "Electro-analysis," 1911 Ed., p. 172).

Removal of Tin Deposits from the Cathode.—The deposit of tin on the platinum cathode may be readily removed by fusing with potassium bisulphate, or dissolving in a mixture of nitric acid and oxalic acid, or by means of dilute hydrochloric acid with a piece of metallic zinc in contact with the cathode (Smith's "Electro-analysis," 1911 Ed., p. 169).

III. *Electrodeposition of Tin by Separate Current.*

On account of the whiteness of tin and it not becoming tarnished by exposure to the atmosphere, an electrolytic deposit of this metal is much desired. There are many uses which could be made of small metallic articles which are coated with an adherent smooth dense bright deposit of tin, but the difficulty of obtaining such a deposit has hindered the larger practice of electroplating with tin.

A number of electrolytes have been suggested, some of which have been patented, but the choice of the proper solution for the coating of articles of iron, steel, copper, brass, or bronze will in most cases largely depend upon the character of the work to be done and the available conditions, such as the source and quantity of current, means of controlling the temperature of the electrolyte, size of the articles, and the method of handling and treating them before and after the electrolysis has been conducted.

The electrolytes which are given below are those which have been recommended and used for electroplating of tin. In many cases the published composition of the electrolytes was given in either ounces or pounds of the ingredients per gallon, but in order to allow ease of comparison of the different solutions, their compositions were calculated into grms. per litre, and temperatures were changed from Fahrenheit into Centigrade.

1. Good deposits of tin may be produced by using an electrolyte containing stannous chloride and acid ammonium oxalate. One litre of this solution is prepared by dissolving 25 to 30 grms. of crystallised stannous chloride in about 400 cc. of water, 55 to 65 grms. of ammonium oxalate, and 3 to 4 grms. of oxalic acid in about 400 cc. of water. Add the oxalate solution to the tin solution with vigorous stirring, so that the white precipitate which forms at first will dissolve. Dilute 1 litre and boil a few minutes. The deposits formed from this electrolyte are said to be excellent, and, further, the anodes corrode normally, so there is no need of adding tin salt to the electrolyte from time to time. This solution has the advantage that it can be mixed with a similarly prepared copper solution, and the mixed solution used for depositing a coating of bronze (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Field's "Principles of Electroplating," 1911 Ed., p. 213).

2. Roseleur's tin bath is recommended as giving the most satisfactory deposits of any of the generally used electrolytes. It is prepared by dissolving 10 to 12·5 grms. of sodium pyrophosphate in 1 litre of water and suspending 1 to 1·5 grm. of fused stannous chloride in the solution by placing it in a copper screen or in a linen bag. Agitate till all the tin chloride is dissolved. The solution is at first cloudy, but finally becomes clear and is ready for use. Voltage required from 1·5 to 4 volts. Use pure tin anodes.

It is stated that any metal may be coated with tin in this solution, the deposit having a dead white lustre resembling silver, which may be polished by either scratch-

brushing or by burnishing. Articles of zinc, copper, brass, and bronze may be directly tinned in this bath, but those of iron and steel must be first tinned in an immersion solution (see I., 2) or else electro-coppered, then scratch-brushed, and finally placed in the tin bath (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Watt and Philip, "Electroplating and Electrorefining," 1911 Ed., p. 344; Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 439).

The Roseleur electrolyte is the one most generally used for electro-tinning. It is capable of giving the whitest deposit of any of the tinning baths which are in general use. The objections to it are that it must be worked hot, that heavy deposits cannot be obtained except after a period of several hours, and that the anodes do not dissolve normally, which necessitates that a concentrated solution of tin chloride be added to the working solution from time to time.

The Roseleur bath has been modified in concentration by other electroplaters:—Weiss used a solution containing 1 grm. of fused stannous chloride and 5 grms. of sodium pyrophosphate per litre (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249). A solution recommended as giving excellent results is prepared by dissolving 15 grms. of sodium phosphate crystals in 1 litre of water, and adding 7·5 grms. tin chloride. Work at low current density (*Metal Industry*, 1906, iv., 138). Another solution, said to have been recommended by eminent authorities, contains 37 grms. sodium phosphate crystals and 20 grms. fused tin chloride per litre. The tension required for this electrolyte was given as 1 to 1·5 volt, when worked hot (*Metal Industry*, 1907, v., 376).

3. An electrolyte which gives good results when electrolysed at ordinary temperature is prepared by dissolving 15 grms. of ammonium chloride and 30 grms. of fused stannous chloride in a litre of water. Use pure tin anodes, and regulate the current so as to avoid pulverulent deposits (*Metal Industry*, 1911, ix., 519).

4. An electrolyte which is strongly recommended as giving excellent results is prepared by dissolving 45 grms. of diammonium stannic chloride per litre of water. Electrolyse at tension of about 1·5 volt (*Metal Industry*, 1907, v., 376).

5. A good lustrous deposit of tin may be produced by using an electrolyte prepared by dissolving 30 to 60 grms. of cream of tartar (potassium hydrogen tartrate) in a litre of water, and adding 7·5 to 15 grms. of tin chloride crystals. Use pure tin anodes, and electrolyse at temperature not less than 70° C. at E.M.F. of 3 to 5 volts. A good lustrous deposit can be obtained in twenty to thirty minutes; scratch-brush with a soft steel brush, or polish on a soft buff wheel, using Vienna lime and kerosene. Keep the solution between 5° and 6° B. (*Metal Industry*, 1908, vi., 162, 227; 1909, vii., 227).

6. A solution which has been used considerably for tinning articles of iron, steel, and brass is prepared by dissolving 60 grms. of caustic soda in about 800 cc. of water, and 22·5 grms. of fused stannous chloride in small amount of water, then pour the tin solution into the caustic solution and dilute to 1 litre. Electrolyse cold, using pure tin anodes, and potential of 1 to 1·5 volt (Bedell's ("Practical Electroplating," 1909 Ed., p. 143). If the solution becomes impoverished in tin it should be revived by adding fused stannous chloride. If solution assumes a milky appearance, add caustic soda until it clears. Keep at about 11° B.

While the work is being plated it takes on a frosty appearance which is usually porous; the work should then be removed from the bath and scratch-brushed. This may have to be repeated several times, if thick deposits are desired. When mechanical plating-barrels are used scratch-brushing will not be necessary, as the rolling and the rubbing of the articles cause them to become burnished. Articles of iron and steel must first be given a slight coating of copper in a copper cyanide electrolyte, preferably hot.

7. A tin bath which has given satisfaction is prepared by dissolving 12 grms. of metallic tin in hydrochloric acid, evaporating to expel the free acid, then adding to a solution of 25 grms. of potassium hydroxide, and diluting to 1 litre. The addition of stannous chloride must be made from time to time as needed (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 330).

8. Elsner used an alkaline electrolyte which he recommends as having given satisfaction for electro-tinning iron and steel. It was prepared by adding 25 grms. of tin tetrachloride to 1000 cc. of water and adding sufficient caustic potash to give a clear solution. He used cast tin anodes, and required a potential of 3 to 5 volts (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

9. Hearn prepared an electrolyte which he used for general work by dissolving 21 grms. of tartaric acid and 30 grms. of caustic soda in 1 litre of water, then adding 3 grms. of fused tin bichloride (McMillian Cooper, "Electrometallurgy," 1910 Ed., p. 249).

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

The Aroma of Coffee.

The tonic and stimulating properties of coffee have been known for a long time, Learned men attribute all the virtues of this precious produce to caffeine. But M. Gabriel Bertrand, of the Pasteur Institute, after a certain number of researches undertaken in collaboration with M. Weisweiller, has just discovered that an infusion of coffee owes it aroma, not only to caffeine, which has been studied for a long time past, but also to the presence of a volatile alkaloid recognised by chemists as being *pyridine*, the smell of which, however, in the mass, is disagreeable. It is probable that the infusion of coffee owes a part of its physiological action to pyridine, of which it contains a proportion corresponding to a quarter of a grm. per kilogrm. of coffee.

M. Gabriel Bertrand has observed that by adding caffeine to boiling sugared water, the aroma of coffee is obtained, but if to this decoction some pyridine is added, in a proportion equal to that which is normally contained in coffee, the aroma of the coffee immediately becomes much stronger. It would seem then that traces of pyridine increase the aroma of coffee.

Different varieties of coffee contain variable proportions of pyridine. The quantity of pyridine contained in a kilogrm. of coffee varies from 200 milligrms. to 250 milligrms.

The Presence of Boron in Milk and in Eggs.

The researches that Messrs. Gabriel Bertrand and H. Agulhon, of the Pasteur Institute, have already published concerning the presence of boron in the human organism, have demonstrated that, contrary to what had been sustained formerly, not only this metalloid exists in the animal organism as well as in vegetables, but moreover there is every reason to suppose and admit its normal presence in every degree of the zoological scale.

Following on these results, the same authors have come to think that boron may perhaps be a fundamental element of the living cellule, if, like iron and magnesia, it plays an indispensable part in nutrition exchanges. This question has led them to complete their statical researches by the examination of milk and of birds' eggs. The fact is there is some reason to suppose that if boron really possesses a cellulary importance, it must already exist in the first stages of life; that it must consequently exist in milk—that liquid that has to supply in itself alone, for a considerable period, all the alimentary requirements of the young mammifer. Likewise, boron must also be found in eggs, that is to say in a state of development, in which it is not necessary to take into considera-

tion the contamination of the organism by exterior contributions.

Now, concerning four species of milk (woman's, ass's, goat's, cow's) collected in the presence of the above-named authors, into vessels cleaned by them, the immediate research for boron each time gave them distinct results.

They have likewise discovered the presence of boron in birds' eggs. So, they conclude, that in all probability boron is to be classed along with other catalytic elements of the living cell.

The Subterraneous Waters of Egypt.

Dr. Roux, the Director of the Pasteur Institute, has lately communicated to the Academy of Sciences a very interesting work of M. Audebean Bey, concerning the subterraneous waters of Egypt. This study gives a classification of the grounds from the point of view of their permeability.

The Chief Engineer of the Egyptian State Domains explains the differences that are remarked in the permeability of the soil in the valley of the Nile, by the deposits of various sorts, due to the divagations of the sinuosities of the branches of the river and of the natural canals during the pleistocene period, and by the changes effected in the dykes and the breaches of the ancient inundation basins in the course of the centuries during which lasted the system of submersion of flooding, &c.

M. Audebean Bey shows that with the works of mechanical draining, which are at present being undertaken in the North of Delta, it will be possible to give to the soil in that region, to-day waste and uncultivated, the fertility it possessed during the Grecian-Roman period, and perhaps even that of the most remote times. He adds also that when the time has arrived, it will be easy to drain and dry the lakes that lie along the Mediterranean coast and to cultivate the vast superficies they occupy.

The Presence of Rare Metals in Mineral Waters.

M. Jacques Bardet has made a whole series of researches concerning the presence of metals in mineral waters. These experiments, made by means of a spectrograph, have led the author to discover in mineral waters the presence of a large number of metallic elements that were entirely unsuspected; amongst others that are very frequent, that of germanium and of gallium, bodies the existence of which had up till now only been remarked in very rare minerals.

MISCELLANEOUS.

American Chemical Society.—*Rochester Meeting.*—The forty-eighth annual meeting of the American Chemical Society will be held in Rochester, New York, September 9th to 14th, inclusive. A meeting of the Council will be held on Monday night, September 8th, at the Hotel Seneca, immediately following a complimentary dinner to be given to the Council at seven o'clock. The programme will open with a general meeting on Tuesday at 10 a.m., in the Assembly Hall at Kodak Park. Members should make a special effort to be present at this opening meeting, as it will not only be one of the most interesting meetings of the session, owing to the fact that it will contain the general addresses, but the whole day will be one of special features, inasmuch as the members of the Society are to be the guests of the Eastman Kodak Company at luncheon following the morning meeting, and the afternoon will be spent in visiting their immense plant at Kodak Park. As the Eastman Company is making special efforts to entertain the membership, it is hoped that every member will endeavour to be present at this first session. A smoker will be held at 8.30 p.m., Tuesday, in Masonic Hall. The divisional meetings on Wednesday, all day, and Thursday and Friday mornings, will be held in the Eastman Building, University of Rochester. The President's address will be given at the East High School, Rochester, at 8 p.m., Wednesday; and the subscription banquet, Thursday night, at 7 p.m., at Powers Hotel. On Thursday and Friday afternoons, excursions will be open to the following manufacturing plants:—Bausch and Lomb Optical Co., Taylor Instrument Co., Curtice Bros. Co., J. Hungerford Smith Co., Moerlback Brewery, German-American Button Co., Genessee Reduction Co., Municipal Incinerator, Stecker Lithographic Co., and possibly others. The only opportunity to visit the Eastman Kodak Company will be on Tuesday afternoon. There are already signs that the meeting this September will be the largest that the Society has ever held as a separate organisation, and it is probable that from 700 to 1000 chemists will be present. All papers for the meeting must be in the Secretary's hands on or before August 22nd, or in the hands of secretaries of divisions by August 20th, in order to be on the programme; especially the secretary of the Organic Division requests that organic papers be sent direct to him.

Institute of Chemistry.—*Pass List: June—July (1913) Examinations.*—Of thirty-three candidates who presented themselves for the Intermediate Examination, sixteen passed:—R. L. Amoore, R. O. Bishop, A. Dingwall, J. W. Donaldson, B.Sc. (Edin.), J. G. Duncan, A. Dunsmore, J. S. Frith, Peter Kerr, B.Sc. (Edin.), K. G. Lochhead, J. W. Lorimer, H. V. Parker, B.A. (Cantab.), H. C. Reynard, F. Smith, F. W. Snelgrove, B.Sc. (Lond.), A. R. Steele, and A. F. Weiss, B.Sc. (Lond.). Of forty-five candidates who presented themselves for the Final Examination, twenty-four passed. In the Branch of Mineral Chemistry:—B. Campbell, B.Sc. (Lond.), J. A. Pickard, B.Sc. (Lond.), A.R.C.S. (Lond.), E. A. Rayner, B.Sc. (Lond.), and E. W. Skelton, B.Sc. (Lond.); in the Branch of Metallurgical Chemistry: R. J. Dunn, B.Sc. (Birm.); in the Branch of Physical Chemistry: (Miss) G. Thompson, B.Sc. (Lond.); in the Branch of Organic Chemistry: J. S. Bainbridge, B.Sc. (Leeds), A. L. R. Clarke, B.Sc. (Lond.), A. Cunningham, B. B. Dey, M.Sc. (Calcutta), J. R. Gray, G. N. Grinling, E. S. Hawkins, B.Sc. (Birm.), P. C. R. Kingscott, A.R.C.S. (Lond.), D. E. Sharp, B.Sc. (Aberdeen), T. F. Smeaton, E. W. Smith, B.Sc. (Lond.), and R. Wheatley, B.Sc. (Leeds); in the Branch of the Chemistry of Food and Drugs, and of Water: (Miss) D. J. Bartlett, H. B. Brown, D. W. Kent-Jones, B.Sc. (Lond.), H. A. Phillips, H. V. Potter, and S. H. Stroud.

Growth of Sponge in Filtering Beds of Waterworks.—An interesting scientific announcement was made recently at a meeting of the Cardiff Waterworks Committee, when the Waterworks Engineer, Mr. C. H. Priestly, said that he, in conjunction with Professor Parker, had succeeded in overcoming the difficulty experienced with regard to the growth of sponge in the pipes in the filtering area at the Llanishen reservoir. The agent employed was a solution of common salt, and so successful had it proved that up to the present week there was no sign of the reappearance of the growth. Mr. Priestly added that Professor Parker himself was so impressed with the result of the experiment that he proposed writing a paper on it to the Geological Society, as a record might prove of assistance to other waterworks encountering similar trouble. The Chairman (Ald. C. H. Bird) said it was very satisfactory to learn that this trouble had at length been got over.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

New Copper Alloy.—We notice in Chemical News, vol. cvii., p. 283, an extract relating to a new copper alloy. Can you inform us how we can obtain samples containing varying proportions of the cobalt-tin alloy? We desire to make some tests with this acid resisting metal.—J. and W. Kearns.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2802.

NOTES ON PLANT CHEMISTRY.

By Dr. P. Q. KEEGAN.

The Bitter Principles.

These principles of plants are neutral, indifferent, and proximate, and have indistinctly marked chemical characters; they seem mostly to be decomposed glucosides of a certain kind, but a few are really lactones. In all cases they arise as direct or indirect products of deassimilation. According to Russell (*Comptes Rendus*, 1904, cxxxix.), the glucosides of the underground parts of plants disappear in spring, and may be present in the stems and leaves only at certain periods, being absent in the adult organs; in some cases they pass over entirely into the central portions of the stem or leaf, while in the flowers they eventually migrate into the seeds. It would seem that these special movements of glucosides are attended by very important chemical transformations which hitherto have been ignored by investigators, the subject of the origin of the bitter principles not receiving that attention which it merits. The ordinary conception of a glucoside is that it is a combination of sugar with an aromatic residue of some kind, but to me it seems difficult to believe that this sugar has at any time been produced independently, and afterwards become combined with a foreign body.

It is much more probable that a hydrolytic scission occurs, with the simultaneous formation of a reducing matter simply derived from the molecule of the glucoside itself, and not necessarily a carbohydrate. However, if we consider the order Labiatæ, we find that while glucosides are rare therein, bitter principles abound in varying proportions. For instance, ground ivy has no tannoid, but it has a bitter principle, and the same is the case with thyme, balm, and various mints; but sage, skull cap, and hemp nettle contain tannoid and little or no amaroid. So also in the order Compositæ various species of Artemisia abound in bitter principles, but have no tannoid or even tannin; where the latter does occur, as in numerous Cynarocephalæ, its quantity is nearly always scanty. Hence it might be suggested that the decomposition of the tannoids would give rise to the bitter principles, and it seems quite possible that certain of the saponins and the alkaloids may originate in some such way. Thus the entire order Umbelliferæ seems to produce caffetannin in considerable quantities without much association of tannoid therewith, the latter in this case being converted into some sort of a poisonous rather than a harmless bitter principle. However, these suggestions are thrown out here mainly as grounds for further research, the actual analyses so far conducted yielding promise of important and interesting conclusions.

The Fat-oil in Plants.

As regards certain aspects this subject has been only superficially studied or considered, although it is of the highest interest and importance. According to Röhmann the fat of animals is not a degenerate product of cell protoplasm, and Gautier states that fat proceeds from the incomplete deassimilation (*i.e.*, by hydration, and not by oxidation) of the animal albumenoids. In plants, however, it is decidedly a product of assimilation which is wanting in no organ. But here the question arises, Is it ever a product of protoplasmic degeneracy? Some authorities seem to think it is so, sometimes at least. For instance, the refractive oily globules which are interposed in the cells where chlorophyll abounds in the winter leaves of ivy, yew, spruce fir, &c., are products of the degradation of the cell plasma due to the lowering of the temperature (Emile Mer); the fat oil which fills he entire cavity of the oleiferous hyphæ in the Amanita genus of fungi seems derived from a fatty degeneration of the protoplasm (Fayod); in autumn the chlorophyll undergoes a kind of oily transformation very comparable to the fatty degeneration which sometimes occurs in animal tissues (Mesnard). On the other hand, as respects the formation of the oil in olives, Spampani declares that it is not a degeneration product of the protoplasm, and this would seem to be the prevalent opinion as to the formation of fat oils in seeds, fruits, and embryonal organs generally. Then, again, there are questions as to whether the fats are derived from the organised living protoplasm or from the dead unorganised proteid? Is the formation of fat direct and straight away; or do fatty acids first make their appearance, and then subsequently combine with glycerol to form fats? It seems to me that the latter is not the case, else more fatty acids would be extracted from the plant by benzene, &c., than what in my experience ever occurs. True, many analysts have concluded that plant fat is rich in unsaturated fat acid, and is thereby distinguished from animal fat; but it is probable that, in some cases at least, these so-called fat acids may have been originally hydrocarbons which oxidise rapidly in the air when removed from the tissues. It would appear, however, that the chief scientific interest of the vegetable oil centres about the origin of chlorophyll. I have already in these notes expressed a hint that chlorophyll cannot be formed in the leaf without the concurrence and assistance of fat-oil. According to Schrotter-Kristelli, "it is probable that by continued reducing action cholesterol yields yellow, and finally green, colouring matters (chlorophyll)." The latter has been recognised as a derivative of pyrolline by Schunck and others, and hence that the basis of blood pigment and of leaf pigment is the same; but it is absolutely certain that the cause and mode of formation of these two substances are entirely different; in fact, it would seem that chlorophyll originates in a way absolutely unique. It is produced within a globule of dense protoplasm which invariably encloses oil as a main ingredient, and which gives off oxygen only in the light. At the same time the globule is alive, *i.e.*, it contains a certain amount of water, and, moreover, as Gautier affirms, the phenomena of dehydration may be produced in the organised and living protoplasm within the cell and never outside of it, and indeed are produced more powerfully in plants than in animals. It is quite conceivable that under all these circumstances a powerful process of dehydration, rendered far more full and complete by the saving presence of oil, would induce the formation of a highly reductive product such as chlorophyll eminently is.

On Ozydases.

The craze of the moment among a certain class of biochemists is what is termed oxydase, a kind of ferment discovered by Bertrand in 1895, although in 1893 Lindet had suspected the existence of something of the kind contained in the crab apple. It is only necessary here to consider some of the evidence on which the existence of a special oxidising agent suppose to operate outside the living organism is based. Lindet states that boiled apple juice remains uncoloured in the air, and that a cooked apple when cut or bruised also does not redden. On the other hand, the fresh white slices may be washed with boiling water till all soluble tannin is removed, and yet as soon as they are exposed to the air they become red. In other words, the boiled extracted juice containing both oxydase and tannin does not colour, because perhaps the ferment is precipitated; but when the slices are practically exposed to the same treatment it does not relinquish its oxidising power, and hence the tissue reddens as if nothing had happened. How in the latter case the oxydase acts is not explained, for undoubtedly the boiling hot water would coagulate and destroy it just as it does in the former case. The truth of the matter, however, seems to be that the juice either within or outside of the apple is, by cooking

or boiling, rendered inert to aerial oxidation, the tannin under these conditions being rendered non-reductive by the action of the acids, &c., present in the liquid; and when the slices are washed with boiling water the whole of the tannic ingredients are by no means removed. In fact, fibro-vascular bundles are profusely scattered throughout the entire tissue of the mesocarp of the apple, and the tannin of the Rosaceæ has a special affinity for vegetable fibre, so much so, indeed, that when once adherent thereto, it cannot be removed by boiling alcohol or water or by dilute caustic soda, as is clearly shown in the analysis of the marsh cinquefoil, &c. There is no organisation in the pressed out juice of fruits, and the supposed action of oxydases on tannins, phenols, &c., therein is not a respiratory phenomenon. In short, the opinion expressed by Gautier in 1897 still holds the field, viz., that "oxidising diastases, being intimately united to the living protoplasm, have not hitherto been distinctly separated therefrom." And the dictum of Pasteur that "oxygen imparts to the cells an activity whence they derive the power of action beyond the influence of free oxygen, in the manner of the ferment-cells," cannot be ignored and is not sufficiently realised. Indeed, the special conditions of the medium are preponderant in these special cases of oxidising energy, and an aldehyde may act in a way hardly distinguishable from that of an oxydase, provided only that the conditions are favourable. But at bottom it is very questionable if the respiratory phenomena of the living organism depend on anything at all but its own inherent vital energy.

The Bearberry (Arbutus uva-ursi).

The glamour of romance, I having seen this plant carpetting the rocky bed of a wild sequestered valley in the Scottish Highlands, superadded to a touch of scientific curiosity, induced me to analyse the leaves thereof. Several analyses of these organs have already been published, one of which reports the presence of much gallic acid; Meisner states that there is 1·2 per cent gallic acid and 36·4 tannin, which latter figure is brought down to 14 by another analyst; in 1898 Perkin isolated therefrom gallotannin, and also gallic and ellagic acids; he thinks also that their colouring matter is quercetin and probably myricetin. Do these analyses exhibit aromatic substances already preformed, or do some of these latter become evolved by a specially violent method of treatment? Having extracted the powdered leaves with boiling benzene, they were then boiled twice with strong methyl alcohol, and the aqueous solution of these latter extracts was tested for tannins, &c., as usual. The result was quite conclusive as regards gallotannin; there was also a clear indication of a tannoid in no respect different from quercitrin; but the reactions of gallic or ellagic acids were not forthcoming. On fusing a portion of the extract with potass there were found pyrogallol and a quantity of phloroglucol much too large for the quantity of gallotannin acted upon, and hence the presence of a tannoid was so far confirmed. Another remarkable feature of these leaves was that, although they had been gathered some nine months previous to analysis, they still retained a notable amount of starch, but no oxalate of calcium was obtained, and the arbutin had all disappeared. The analysis proved very interesting in other respects. It is known that in the Central Alps a near relative, viz., *A. alpina*, assumes in autumn a vivid scarlet coloration, one of the most beautiful reds of any autumnal foliage of the world; but it is difficult to understand how this pigment proceeds from gallotannin as a chromogen. In fact, I have myself seen an extremely fiery red autumn tint on a species of azalea which contained only an iron-greening, phlobaphenic, catechol-phloroglucin tannin, according to my own analysis. Again, a member of that band of botanists who classify plants on the basis of evolution and anatomy, but reject chemistry, has recently suggested that the bilberry, bearberry, &c., should be removed from the order Ericaceæ (heaths) altogether. Now, there is no gallotannin in the bilberry, or in the heather. In an analysis published by Kanger in 1902 of the cowberry he reports the presence of gallic and ellagic acids, not as such, but as arising by the decomposition of the tannin, which he says on potass-fusion or dry distillation yields quinol, but this phenol almost certainly arises from arbutin (not always present), and not from tannin. I found that in the products of potass-fusion of the tannins of the azaleas and of bilberry respectively, the phloroglucol was in excess in the former case, *i.e.*, in the case where the autumnal red is excessively vivid, whereas with the bilberry the protocatechuic acid was predominant.

Patterdale, Westmorland.

PREPARATION OF THE NITRITES OF THE PRIMARY, SECONDARY, AND TERTIARY AMINES BY THE INTERACTION OF THE HYDROCHLORIDES OF THE BASES AND ALKALI NITRITES.

Explanation of the Action of Nitrous Acid on the Amines.

(Part I.).

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry, Government College, Rajshahi, Bengal, India.

(Concluded from p. 55.)

Steam Distillation in Vacuum.

The temperature of the bath was maintained at 80° to 85°. One grm. of the hydrochloride gave as the first distillate measuring 202 cc., which contained 0·38 grm. of benzylammonium nitrite. The solution was neutral to litmus and contained no nitrate. There was a faint smell of benzyl alcohol. 100 cc. of the first distillate when crystallised in four vacuum desiccators gave white deliquescent crystals of benzylammonium nitrite, soluble in water and alcohol.

0·1376 gave 24·4 cc. N_2 at 29° and 754 mm. (made up to 10 cc., of which 2½ cc. = 6·1 cc. N_2); hence N ("nitritic") = 9·5 per cent. $C_6H_5.CH_2.NH_2.HNO_2$ requires N ("nitritic") = 9·0 per cent.

The solid nitrite was also obtained after concentrating the distillate on the water-bath to a small bulk. 200 cc. of the distillate was evaporated to 5·2 cc. only, when 62·8 per cent of the benzylammonium nitrite still remained in the solution. 310 cc. of the distillate was evaporated to 26·2 cc., when 84·5 per cent of the nitrite remained as such. The crystals of benzylammonium nitrite thus obtained were contaminated with small quantities of benzyl alcohol.

Interaction between Piperidinium Hydrochloride and Sodium or Potassium Nitrite. Sublimation in Vacuum

One or 2 grms. of the hydrochloride purified from absolute alcohol (Cl = 29·8 per cent found, Cl = 29·2 per cent calc.) were taken and mixed as usual with sodium or potassium nitrite. The temperature of the bath was maintained at 50° during the evaporation to dryness. No gas collected in the nitrometer. When the liquid was completely evaporated to dryness the neck of the flask was raised, and the temperature was also raised to 75° to 80°. A very small quantity of white crystals was observed to sublime in the cooler parts of the neck of the flask. The temperature was not allowed to rise above 90°. No gas collected in the nitrometer. The liquid in the test-tube also contained nitrite. The sublimate was washed out and tested, then mixed with the distillate in the test-tube and crystallised in the vacuum desiccator, when colourless deliquescent crystals of piperidium nitrite were obtained free from chloride.

Next, the water-bath was substituted by a sulphuric acid bath, and the temperature raised to 100° and above. The salt in the neck of the flask melted, and gradually

was turned into a reddish yellow liquid which readily gave Liebermann's nitroso-reaction. This liquid was therefore nitroso-piperidine, and, as pointed out before (Neogi, *Trans. Chem. Soc.*, 1911, xcix., 1600), is obtained by the decomposition of piperidinium nitrite according to the following equation :—$C_5H_{11}N.HNO_2 = C_5H_{10}N.NO + H_2O$. No gas collected in the nitrometer.

Steam Distillation in Vacuum.

Using 1 grm. of the hydrochloride the first distillate, 210 cc., contained 0·46 grm. of the nitrite, distillation being effected at 70°, almost quantitative yield being obtained in 520 cc. of the distillate. The solution can be evaporated to a small bulk without appreciable decomposition. 230 cc. of the distillate were evaporated to 26·5 cc., which contained 92·6 per cent of the nitrite undecomposed. The solution when crystallised in a vacuum desiccator gave deliquescent crystals of piperidinium nitrite, readily soluble in water and alcohol, and almost insoluble in ether (Neogi, *Trans. Chem. Soc.*, 1911, xcix., 1600).

0·0874 gave 18·0 cc. N_2 at 27° and 760 mm. (made up to 10 cc., of which 2 cc. = 3·6 cc. N_2); hence N_2 ("nitritic") = 11·2 per cent. $C_5H_{11}N.HNO_2$ requires N_2 ("nitritic") = 10·6 per cent).

In this way from 1 grm. of the hydrochloride from 0·4 to 0·6 grm. of the nitrite can easily be prepared.

Methylammonium Hydrochloride and Sodium or Potassium Nitrite.

The nitrites of the primary, secondary, and tertiary alkylamines are less stable than the nitrites described before. Of these nitrites, however, diethylammonium nitrite and triethylammonium nitrite sublime when heated in a vacuum with or without decomposition. Other nitrites of this series decompose more or less readily in the solid or liquid condition when heated in a vacuum. The following experiments show that, though these nitrites in the solid or liquid condition are more or less unstable, they are fairly stable *in solution*, and, in fact, this solution may be concentrated on the water-bath without great loss.

Steam Distillation in Vacuum.

The hydrochloride was as usual exhausted with small quantities of absolute alcohol and analysed (Cl = 52·1 per cent found, Cl = 52·6 per cent calc.).

There was scarcely any action on mixing. The temperature of the bath was maintained between 55° and 60°. Using 1 grm. of the hydrochloride the first distillate amounting to 215 cc. contained 0·52 grm. of methylammonium nitrite. There was no chloride or smell of alcohol in the distillate, which was neutral to litmus. The mercury level in the manometer remained almost constant, showing that very little decomposition took place. The solid nitrite was obtained as deliquescent, colourless crystals slightly tinged greenish, by evaporating 100 cc. of the first distillate to dryness in four vacuum desiccators. The solid nitrite was also obtained after concentrating the distillate on the water bath. 180 cc. of the distillate containing 0·44 grm. of the nitrite when concentrated to only 11·2 cc. still contained 81·2 per cent of nitrite. When this concentrated solution was crystallised in a vacuum desiccator the solid nitrite was obtained in a fairly pure condition, only contaminated with very small quantities of the nitrates. As the decomposition product of methylammonium nitrite is methyl alcohol which is dissolved in the sulphuric acid of the desiccator, this rapid method of obtaining the nitrite is recommended as a method of preparation.

0·1392 gave 44·0 cc. N_2 at 30° C. and 755 mm. (made up to 10 cc., of which 1 cc. = 4·4 cc. N_2); hence N_2 ("nitritic") = 17·1 per cent. $CH_3.NH_2.HNO_2$ requires N_2 ("nitritic") = 18·0 per cent.

Ray and Rakshit (*Trans. Chem. Soc.*, 1911, xcix., 1018) have shown that methylammonium nitrite decomposes mainly into methyl alcohol and nitrogen. These are also the products of the interaction of nitrous acid and methylamine, so that methylammonium nitrite is evidently the intermediate compound in this interaction, which decomposes according to the equation—

$$CH_3.NH_2.NHO_2 = CH_3.OH + N_2 + H_2O.$$

Interaction between Ethylammonium Hydrochloride and Sodium or Potassium Nitrite.

The method of preparation and decomposition of the nitrite of this primary amine is identical with that of methylamine. There was no action when cold solutions of ethylamine hydrochloride (Cl = 42·8 per cent found, Cl = 43·5 per cent calc.) and sodium or potassium nitrite were mixed. The temperature at which distillation was conducted was 55° to 60°. The distillate contained no chloride or alcohol and was neutral in reaction. Two grms. hydrochloride yielded 0·69 grm. of the nitrite in the first distillate amounting to 160 cc. The liquid nitrite was obtained by evaporating 100 cc. of the first distillate in four vacuum desiccators without previous concentration as a colourless liquid slightly tinged yellow, readily soluble in water and alcohol.

0·1542 gave 43·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc. with water, of which 1 cc. = 4·3 cc. N_2); hence N_2 ("nitritic") = 14·9 per cent. $C_2H_5.NH_2.HNO_2$ requires N_2 (nitritic") = 15·2 per cent.

The liquid nitrite was also obtained after concentrating the distillate on the water-bath. 224 cc. of the distillate was concentrated to 27·2 cc., when 84·6 per cent of the nitrite remained as such, the rest either evaporating with the steam or decomposing. As the principal decomposition product of ethylammonium nitrite is ethyl alcohol which is absorbed in the vacuum desiccator, the nitrite thus obtained was practically pure, containing small quantities of the nitrate.

The products of decomposition of ethylammonium nitrite (Ray and Rakshit, *Trans. Chem. Soc.*, 1911, cxix., 1472) are mainly ethyl alcohol, nitrogen, and water, which are also the end-products of the interaction of nitrous acid and ethylamine. Evidently the end-products are the decomposition products of ethylammonium nitrite, which decomposes according to the equation—

$$C_2H_5.NH_2.HNO_2 = C_2H_5.OH + N_2 + H_2O.$$

Interaction between Dimethyalmmonium Chloride and Sodium or Potassium Nitrites.

The preparation of the nitrites of two secondary alkylamines was then undertaken. Dimethylammonium nitrite is a liquid and comparatively unstable (Ray and Rakshit, *Trans. Chem. Soc.*, 1911, xcix., 1472), while diethylammonium nitrite is a solid, and sublimes unchanged when heated in a vacuum (*Trans. Chem. Soc.*, 1912, ci., 612).

Steam Distillation in Vacuum.

Two grms. of dimethylammonium chloride purified from alcohol (Cl = 43·9 per cent found, Cl = 43·7 per cent calc.), 1 grm. gave 0·56 grm. of the nitrite in the first distillate amounting to 120 cc., distillation being conducted at 55° to 60°. When 100 cc. of the distillate was kept in four vacuum desiccators as described above, dimethylammonium nitrite was obtained as a pale yellow liquid, very soluble in water and alcohol.

0·1848 gave 50·5 cc. N_2 at 30° and 753 mm. (made up with water to 10 cc., of which 2 cc. = 10·1 cc. N_2); hence N_2 ("nitritic") = 14·7 per cent. $(CH_3)_2.NH.HNO_2$ requires N_2 = 15·2 per cent.

150 cc. of the distillate containing 0·303 grm. of the nitrite was evaporated to 10·2 cc., when 64·2 per cent of the nitrite was found to be present. The liquid nitrite thus obtained was contaminated with small quantities of the nitroso-compound.

The principal decomposition product being nitroso-dimethylamine (*Trans. Chem. Soc.*, 1912, ci., 612), it is evident that dimethylammonium nitrite is an intermediate compound in the interaction between nitrous acid and dimethylamine.

Interaction between Diethylammonium Chloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

It has already been mentioned that diethylammonium nitrite is a stable salt, and sublimes unchanged when heated in a vacuum. Ray and Rakshit have not determined the temperature at which sublimation of the pure nitrite takes place nor the temperature at which decomposition of the salt commences. When heated in a vacuum the nitrite commences to sublime in colourless crystals at 55°, and at 55° to 65° a good quantity collects in the cooler parts of the tube. When the temperature is further raised the salt melts at 74° to 76° into a pale yellow liquid which solidifies on cooling. If, however, the temperature is raised to 90° and above, a pale yellow oil is obtained which does not solidify on cooling and which is insoluble in water. This liquid gives nitroso-reaction, and is evidently nitroso-diethylamine.

Sublimation in the Töppler vacuum with 2 grms. of the hydrochloride (Cl = 32·8 per cent found, Cl = 32·4 per cent calc.) mixed with sodium or potassium nitrite does not give good results, only very small quantities subliming at 60° to 65°. The liquid in the test-tube, however, gave tests of the nitrite.

Steam Distillation in Vacuum.

Almost quantitative results are, however, obtained by submitting a solution of the mixture to vacuum distillation in steam.

0·5 grm. of the hydrochloride gave 0·38 grm. of the nitrite in 216 cc. of the distillate. Using 2 grms. of the hydrochloride 280 cc. of the distillate gave 0·72 grm. of the nitrite, which was evaporated to 7 cc. only on the water-bath, when 88·3 per cent of the nitrite remained as such. The temperature at which distillation was carried on was 65° to 70°. The preparation of the solid nitrite in a pure condition can be very easily done after concentrating the distillate on the water-bath to about 25 cc. The crystals were white, deliquescent, very soluble in water and alcohol. No nitroso-compound accompanied the crystals.

0·1062 gave 23·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc., of which 2 cc. = 4·6 cc. N_2); hence N_2 ("nitritic") = 11·62 per cent. $(C_2H_5)_2.NH.HNO_2$ requires N_2 ("nitritic") = 11·66 per cent.

The main decomposition product of diethylammonium nitrite being nitroso-diethylamine, which is also the end-product of the interaction of diethylamine hydrochloride and alkali nitrite, it is evident that diethylammonium nitrite is the intermediate compound hitherto not isolated from the mixture.

Interaction between Trimethylammonium Chloride and Sodium or Potassium Nitrite.

Of the nitrites of the two tertiary amines examined, triethylammonium nitrite is a stable compound which sublimes on heating in a vacuum though with decomposition. Trimethylammonium nitrite does not sublime in a similar manner.

Steam Distillation in Vacuum.

The distillation was conducted at 55° to 60°, 2 grms. of the hydrochloride (Cl = 37·8 per cent found, Cl = 37·2 per cent calc.) being used. 160 cc. gave 1·1 grm. of the nitrite, almost quantitative yield being obtained in 450 cc. The pure nitrite was obtained on crystallisation of 100 cc. of the distillate in four vacuum desiccators at the temperature of the laboratory.

0·1300 gave 29·7 cc. N_2 (made up to 22 cc., of which 2 cc. = 2·7 cc. N_2) at 30° and 755 mm.; hence N_2 ("nitritic") = 12·21 per cent. $(CH_3)_3N.HNO_2$ requires N_2 ("nitritic") = 13·20 per cent.

On evaporating 210 cc. of the distillate containing 1·0 grm of the nitrite to 18 cc., 61·1 per cent of the nitrite remained as such. Appreciable quantities of the nitrate accompanied the nitrite.

It is incorrect to suppose, as is generally done, that there is no reaction between nitrous acid and a tertiary amine. What such statement really means is that no specific reaction takes place other than what usually takes place between nitrous acid and a base, the corresponding nitrate and nitric oxide being formed by the decomposition of the unstable nitrous acid according to the equation $3HNO_2 = HNO_3 + H_2O + 2NO$, the nitric acid combining with a part of the free amine.

In order to corroborate this statement, 1 grm. of the hydrochloride mixed with molecular quantities of sodium nitrite was dissolved in a small quantity of water and evaporated to dryness, using the apparatus described before for sublimation *in vacuo*. The solution was evaporated to dryness at 50°; very little gas collected in the nitrometer. The temperature was then raised to 60° and then to 70°. A gas collected in the nitrometer which consisted mainly of nitric oxide mixed with small quantities of nitrogen and the vapours of the free amine. The distillate in the test-tube was strongly alkaline in reaction and smelt of trimethylamine, and also contained a mixture of the nitrite and nitrate.

The formation of the decomposition products can very readily be explained in the following manner:—During the interaction trimethylammonium nitrite is formed, which distils in vacuum with the steam in small quantities as such. Part of the trimethylammonium nitrite, however, dissociates into the free amine and nitrous acid,—

$$(CH_3)_3N.HNO_2 = (CH_3)_3N + HNO_2.$$

The nitrous acid again decomposes into nitric acid and nitric oxide, according to the equation given above, the nitric acid combining with a portion of the free amine forming the nitrate, while part of the free amine remains uncombined.

The decomposition of pure trimethylammonium nitrite has been studied by Ray and Rakshit (*Trans. Chem. Soc.*, 1911, xcix., 1474), who have found that the same decomposition products, viz., the nitrate, the free amine, and nitric oxide, are obtained.

Interaction between Triethylammonium Chloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

One or 2 grms. of the hydrochloride purified from alcohol (Cl = 26·7 per cent found, Cl = 25·9 per cent calc.) were used with sodium or potassium nitrite. The solution was evaporated to dryness at 50° without decomposition. The temperature was then gradually raised to 70° and then finally to 90°. The evolution of gas was very brisk. The gas was found to consist mainly of nitric oxide with small quantities of nitrogen. No appreciable sublimation was observed, as water being one of the products of decomposition the small quantity that usually sublimed was dissolved in the water. The distillate in the test-tube was strongly alkaline and strongly smelt of the free amine. Besides the amine, the distillate contained nitrite mixed with the nitrate. Here, as in the case of trimethylamine, the principal products of the interaction of nitrous acid and the tertiary amine are free amine, nitrate, and nitric oxide. The explanation is also the same, viz., that triethylammonium nitrite is formed, part of which distils unchanged with the steam and part dissociates into triethylamine and nitrous acid, the latter decomposing into nitric oxide and nitric acid, which forms the nitrate.

The decomposition of pure triethylammonium nitrite has been studied by Ray and Rakshit (*Trans. Chem. Soc.*, 1912, ci., 218), who have found that the same decomposition products are obtained along with small quantities of nitrous oxide and alcohol.

Vacuum Distillation in Steam.

The temperature at which distillation was conducted was 65° to 70°. One grm. hydrochloride gave, in 180 cc. distillate, 0·48 grm. of the nitrite. 230 cc. of the distillate was evaporated to 28·5 cc. on a water-bath, when 92·2 per cent of the nitrite remained undecomposed. The crystals obtained from the concentrated liquid were white,

deliquescent, very soluble in water and alcohol. The nitrite was also obtained in a pure condition on concentrating 100 cc. of the distillate in four vacuum desiccators at ordinary temperature.

0·1116 gave 19·2 cc. N_2 at 30° and 754 mm. (made up to 10 cc. with water, of which 2½ cc. = 4·8 cc. N_2); hence N_2 ("nitritic") = 9·2 per cent. $(C_2H_5)_3.N.HNO_2$ requires N_2 ("nitritic") = 9·4 per cent.

Both trimethyl- and triethyl-ammonium nitrites are slowly changed into the nitrate on keeping as a result of their dissociation.

Interaction between Tetramethylammonium Nitrite and Sodium or Potassium Nitrite. Vacuum Distillation in Steam.

While attempting to prepare the nitrites of tetralkylammonium bases, it was found that tetramethylammonium nitrite does not volatilise with steam in vacuum, though the distillation was carried on at varying temperature from 60° to 100°. Work on other amines is in progress.

Chemical Laboratory, Government College,
Rajshahi, Bengal, India.

MELTING-POINTS OF THE REFRACTORY ELEMENTS.*

I. Elements of Atomic Weight from 48 to 59.

By G. K. BURGESS and R. G. WALTENBERG,
Bureau of Standards.

The elements included in this list are the iron group: nickel, cobalt, iron, manganese, and chromium, and also vanadium and titanium. In subsequent papers results will be given on other refractory elements now being studied, and it is hoped eventually to include all the available refractory elements in this series of melting-point determinations. The method mainly used is that of the micropyrometer, which, with substances that melt sharply, as nickel, cobalt, and iron, permits working to a precision of 1 or 2° with a few thousandths of a milligrm. of the material. ("A Micropyrometer," by G. K. Burgess, *Journ. Washington Academy of Sciences*, 1913, iii., 7; *Phys. Zeit.*, 1913, xiv., 158; *Bull.* Bureau of Standards, 1913, ix., 475.)

An estimation of the melting-points of the iron group elements was made some years ago by a similar but less sensitive method at a time when none of these melting-points was well known. ("Melting-points of the Iron Group Elements by a New Radiation Method," by G. K. Burgess; *Bull.* Bureau of Standards, 1907, iii., 345.) The object of these earlier measurements was primarily to demonstrate the convenience and reliability of the method, especially for those elements which can be obtained pure only in minute quantities. It is believed that the present series of determinations, with the improved apparatus, will contribute to a more exact knowledge of these melting-points. The melts were made for the most part in pure hydrogen, and except for titanium, were taken on platinum strips 6 to 8 cm. long, 4 mm. wide, and 0·01 or 0·02 mm. thick. Manganese was also melted on nickel strips and titanium was melted on iridium strips.

Calibration with Nickel and Palladium.—For melts on platinum the pyrometer was calibrated in terms of the melting-points of nickel and palladium. The melting of these metals is extremely sharp on platinum and they appear to show no alloying until they melt. It is assumed that they melt on platinum at the same temperatures as in crucibles; this we have found to be the case for nickel, palladium, platinum, and iron. Numerous observations were made with various metals upon the possible effects on the melting-point determinations of alloying with the platinum strip. We are convinced, that except possibly in some cases which we shall not consider here in which there may be a chemical reaction among the materials in the furnace, as for example when silicon, platinum, and hydrogen are together, there is no significant alloying effect with the apparatus and materials as we use them.

The melting-points of both nickel and palladium may be considered as well established by several series of measurements. (See Day and Sosman, Carnegie Institution of Washington, Pub. 157, 1911; Waidner and Burgess, *Bull.* Bureau of Standards, 1907, iii., 163.) We have made an independent optical determination of the nickel melting-point in hydrogen with an Arsem furnace. (*Journ. Am. Chem. Soc.*, 1906, xxviii., 921.) The nickel was melted in a magnesia crucible contained within an out-glazed, closed-end porcelain or kaolin tube. Temperatures were measured with a Holborn-Kurlbaum form of Morse pyrometer which had been calibrated by Dr. Kanolt at the melting-points of antimony (630°), Ag_3Cu_2 (779°), silver (960·5°), copper (1083°), and diopside (1391°). Five observations by Dr. Kanolt on the melting-point of platinum with this pyrometer gave 1755° ± 5 in an iridium furnace, or in exact agreement with the generally accepted value. (See Day and Sosman, *loc. cit.*)

For nickel, four observations gave us 1449°, 1450°, 1449°, 1449° in the Arsem furnace, by the method of optical heating and cooling curves, values which are close to Day and Sosman's value, 1452°. (C. W. Kanolt, Tech. Paper No. 10, Bureau of Standards, 1912.) Four observations of the melting point of nickel on iridium with the micropymeter gave us 1452°.

With the long filament pyrometer lamps used, the equation $\log c = a + b \log T$ (in which c = current and T = absolute temperature and b is very nearly unity) is sufficient for very considerable temperature ranges, and permits a calibration in terms of two temperatures only, *i.e.*, nickel and palladium. (Pirani, *Verh. Phys. Ges.*, 1910, xii., 323.) Applying this equation by extrapolation to the determination of the platinum melting-point by observing the melting of platinum strips mounted as usual for taking metal melts, we obtained 1755° ± 5 from six observations. The values found for diopside (1391°) and anorthite (1549°) by Day and Sosman were also exactly reproduced by us with the micropyrometer.

The metals actually used for calibration in hydrogen were "Kahlbaum" electrolytic nickel (MP = 1452°) and pure Heraeus palladium (MP = 1549°), both of the same grade as used by Day and Sosman. (Day, Sosman, and Allen, *loc. cit.*; the analysis by Dr. Allen of these products gave the nickel as 99 835 pure and the palladium 99·975). A sample of their palladium gave exactly the same melting-point as ours. In controlling the constancy of the pyrometer lamps and studying the reproducibility of the melts some 35 observations were taken of nickel and 20 of palladium. The various metals were not studied in regular order but were mixed as indiscriminately as possible, with observations on the standard points, nickel and palladium.

Iron.—Pure electrolytic iron from three sources and as many different methods of preparation were used, namely, from Prof. C. F. Burgess (99·97 per cent Fe), from Langheim-Pfanhauser Werke A. G. (99·98 per cent Fe), and from a sample (99·99 per cent Fe) prepared by Mr. J. R. Cain of this Bureau. "Kahlbaum" iron in powdered form and iron reduced on the platinum strip in hydrogen from Kahlbaum iron oxide were also used.

Table I.—*Melting-point of Iron in Hydrogen by Micropyrometer.*

Electrolytic, C. F. Burgess,	1538°, 1537°, 1530°, 1534°, 1530°, 1532°
Mean	1533°
Electrolytic, Langheim-Pfanhauser,	1524°, 1532°, 1534°, 1534°, 1535°
Mean	1532°
Electrolytic, Cain	1533°
Powder, "Kahlbaum"	1534°
From Oxide, "Kahlbaum"	1532°

* To appear in the Bulletin of the Bureau of Standards. From *Journal of the Washington Academy of Sciences*, iii., No. 13.

The mean value is 1533° ± 1°. This is somewhat higher than all other recent determinations, which range from 1502° to 1532°. In the Arsem furnace we obtained *in vacuo* 1531°, 1529°, 1531°, 1527°, and in hydrogen 1523° and 1527°.

Cobalt.—The cobalt used was cobalt "Kahlbaum" in the form of powder, Kahlbaum's Würfeln, cobalt reduced in hydrogen on the platinum strip from "Kahlbaum" cobalt oxide, and a sample kindly furnished by Messrs. Day and Sosman, cut from material which had been used for their determinations and which was originally powdered cobalt "Kahlbaum," shown by Dr. E. T. Allen to be 99·951 per cent cobalt. (Day, Sosman, and Allen, *loc. cit.*) The mean is 1477° ± 2.

TABLE II.—*Melting-point of Cobalt by Micropyrometer.*

"Kahlbaum," powder and Würfeln together,	1478°, 1479°, 1482°, 1476°, 1475°, 1476°, 1478°
Mean	1478°
Co from the oxide "Kahlbaum"	1475°, 1478°
Day and Sosman's sample	1474°, 1478°, 1478°

Three observations taken in the Arsem furnace each gave for the melting-point of cobalt 1478°. Finally two melts of cobalt on iridium gave with the micropyrometer 1477° and 1478°. The value of the cobalt point which Day and Sosman found is 1490° in a nitrogen atmosphere.

Chromium.—Strictly pure chromium was not available, and it is difficult to locate exactly the melting-points of an impure viscous substance. Observations were taken on two samples from Kahlbaum and on one from Dr. H. Goldschmidt, all of a purity probably not greater than 98 per cent.

TABLE III.—*Melting-point of* (98 *per cent ?*) *Chromium by Micropyrometer.*

Kahlbaum I.	1527°
Kahlbaum II.	1536°, 1513°, 1513°
Goldschmidt	1514°, 1524°

As the best representative value we may take 1520°. The melting-point of pure chromium, however, may well be above that of iron, as may be shown by a consideration of the well-known formula for lowering the freezing-point by metallic impurities. On the other hand, the value 1520° may be more nearly correct if the oxides present do not lower but raise the chromium melting-point, as was found in the case of vanadium by Ruff and Martin. (Ruff and Martin, "Uber reines Vanadin," *Zeit. Angew. Chem.*, 1912, xxv., 49.) If chromium is melted, for example, in a slightly oxidising atmosphere or in impure hydrogen, an apparent melting-point above that of platinum may be obtained.

Manganese.—We have not been able to obtain pure manganese, and the impure samples from Kahlbaum and from Goldschmidt are even more sluggish than chromium. The Goldschmidt manganese was from a sample of about 97·5 per cent pure. Melts were taken both on platinum and on nickel strips with the micropyrometer, using gold (1063°) and palladium as calibration points. Those on nickel were less satisfactory, due apparently to evaporation of nickel.

TABLE IV.—*Melting-point of* (97·51) *Manganese by Micropyrometer.*

Kahlbaum	on Pt, 1242°; on Ni, 1221°
Goldschmidt..	on Pt, 1261°, 1264°, 1279°; on Ni, 1254°

The mean is 1254°, which is probably lower than the melting-point of strictly pure manganese by 20°.

Vanadium.—Dr. v. Wartenberg, of Berlin, kindly sent us some 97 per cent vanadium prepared by him from the suboxide by the alumino-thermic method with calcium; it contains traces of Ca, Al, and Fe. Professor Wedekind, of Strassburg, also furnished us with a sample of his 97 to 98 per cent vanadium. We have also examined two samples purchased from Kahlbaum at different dates. None of the samples melts sharply, the substance being viscous; all samples show evidences of incipient melting many degrees below the temperature at which the melting is complete.

With the Kahlbaum samples, evidences of melting were apparent as low as 1500°; melting was complete at about 1720°, the samples showing evidences of non-homogeneity of composition.

With Dr. v. Wartenberg's and Professor Wedekind's vanadium the following results were obtained:—

TABLE V.—*Melting-point of* 97 *per cent Vanadium by Micropyrometer.*

97 to 98 per cent V from Wedekind,	1700°, 1757°, 1773°, 1717°
97 per cent V from v. Wartenberg,	1680°, 1691°, 1691° (pieces of about 0·001 mg.), 1685°, 1699°, 1705° (medium-sized pieces), 1725° (largest pieces).

Evidences of incipient melting were apparent at about 1650° with these materials. Other determinations of the vanadium melting-point range from 1680° to 1750°. We would place the vanadium melting-point at about 1720°, both from a consideration of our own and of other determinations.

Titanium.—Prof. M. M. A. Hunter, of Rensselaer Polytechnic Institute, kindly placed at our disposal a sample of pure titanium, which he had prepared from material furnished by the Titanium Alloy Manufacturing Company, of Niagara Falls. This titanium, analysed by Professor Hunter, contains only a trace of iron and no other detectable impurity. Professor Wedekind likewise kindly sent us two samples prepared by him of 94 to 95 per cent purity and one by Dr. v. Wartenberg. The colloid titanium of Wedekind melted at 1508° to 1451°, and his powdered titanium at 1452°. We also took observations on two samples from Kahlbaum, which were evidently quite impure, showing evidences of an extended melting range. For the Kahlbaum samples, the following melting-points were obtained:—1664°, 1724°, 1677°, 1737°, 1641°. The titanium of Hunter and of v. Wartenberg showed no signs of melting on platinum; their melting points were taken on iridium strips.

TABLE VI.—*Melting-point of Titanium by Micropyrometer.*

Ti from Professor Hunter	1790°, 1785°, 1785°
Mean	1788°
Ti from Dr. v. Wartenberg	1778°, 1807°, 1815°
Mean	1800°

These melting-points are fairly sharp, and the location of the temperature was made by calibrating the micropyrometer for the iridium strip by taking observations on it of the melting of palladium (1549°) and of platinum (1755°).

Summary.—We have shown that the micropyrometer may be made an instrument of precision for the determination of the melting-points of refractory metals and salts; that in the case of the metals examined, the effect of alloying of microscopic particles on platinum and iridium is inconsequential until after melting which we have shown for nickel, cobalt, and iron to occur at the same temperature for minute particles on the strips as for considerable quantities in crucibles of magnesia.

Assuming the melting-points of nickel to be 1452°, palladium 1549°, and platinum 1755°, and the calibration curves of the pyrometer lamps of the form $\log c = a + b \log T$, for the range here studied, we have determined the melting-points of Fe, Co, Cr, Mn, V, and Ti with the micropyrometer and of Ni, Co, and Fe in quantity in the electric furnace, all melts having been taken in pure hydrogen and Fe also *in vacuo*. For Cr, Mn, and V, strictly pure materials were not available, and we can but estimate the melting-points of the pure elements.

Table VII.—*Melting points of Elements of Atomic Weight 48 to 59.*

Metal.	Melting-point with micropyrometer.	Purity (per cent).	Probable melting-point of pure element.
Nickel ..	1452° (*a*) 1449 (*b*)	99·835	1452° ± 3
Cobalt	1477 ± 2 1478 ± 1 (*c*)	99·951	1478° ± 5
Iron	1533 ± 1 (*d*) 1528 (*b*)	99·98 ± 01	1530° ± 5
Manganese..	1255	97 to 98	1260° ± 20
Chromium ..	1520	98 to 99	1520° to >Fe
Vanadium ..	1720	97 to 98	1720 ± 20
Titanium ..	1794 ± 12	99·9+	1795 ± 15

(*a*) Assumed value on platinum strip; also observed value on iridium strip.
(*b*) Crucible melts in electric furnace.
(*c*) Crucible melts in electric furnace; also on iridium strip with micropyrometer.
(*d*) Five samples all agreeing to within 3°.

In the complete paper, the method is discussed more in detail and photomicrographs are given showing characteristics of the various melts.

THE INDEX TO CHEMICAL LITERATURE.

By L. H. BAEKELAND.

Under this title, the U.S. Patent Office has published a statement describing the work undertaken by the Classification Division, so as to enable rapid and complete searches to be made on any subject of chemical literature. This is a gigantic piece of work, embracing not merely patent literature, but practically all fields of chemical literature.

(Appendix K of the Report of the Investigation of the U.S. Patent Office, by the President's Commission on Economy and Efficiency, December, 1912. House of Representative, 62nd Congress, 3rd Session, Document No. 1110).

Before the chemical card index was commenced, anything like a complete search of the literature was practically impossible, and the validity of chemical patents was more or less in doubt; for, after the most elaborate search possible was made, a five-line paragraph in the files of some little known chemical journal published in Japanese, Russian, or other not readily understood language, would be sufficient if cited in court to invalidate the granted patent.

It will be several years before this card index is complete, although much assiduous work is being done on it. In the meantime, enough has already been accomplished that any one making a search on the literature of a chemical subject can save much labour and time by consulting the index of the Patent Office. It should be noted that the index is accessible not only to the examiners of the Patent Office, but to patent lawyers practising before the office, as well as to chemists and scientific workers all over the land. Hence, this card index is becoming a national monument to chemical literature.

For those not living too far away a visit to Washington to consult the index may prove the shortest and cheapest way to make a search in chemical literature. It would be highly desirable, however, if duplicates of this index could be obtained for the more important libraries all over the country. It is true that copying this card index would be rather expensive, but there is no doubt that the enormous value of such a copy would be fully worth the expense. Why could not some of the libraries of the country work together and have several copies printed at the same time, and thus distribute the cost of the task among themselves?

It is interesting to quote from the report mentioned above:—

"In planning the chemical card index, since it was manifestly impossible to index all chemical literature, it was decided to cover the work of the past by making a judicious selection of certain works of a general nature, such as the 20 volume work of Gmelin, the annual volumes of the Chemical Society of London, and the 4 volume edition of Watts's 'Dictionary of Chemistry,' Richter's 'Lexicon of Carbon Compounds,' and other works of that character; by indexing these works the literature of the past would probably be as completely covered as it could be by any plan which the office had the force and means available for accomplishing."

"For the future it was proposed to keep the abstract journals of the Chemical Society of London, the German abstract periodicals, *Berichte* and the *Centralblatt*, and other works of that character indexed up to date."

"Later, when the American Chemical Society, in 1907, commenced the publication of its very complete set of abstracts, it was determined to omit the periodicals in German and other foreign tongues, and retain in the card index only the yearly index volume of the Chemical Society of London in addition to the American abstracts."

The above reference to the usefulness of the abstracts of the American Chemical Society would be decidedly more satisfactory if it were not accompanied by the following statement:—

"The question has been raised whether the annual index of the Chemical Society of London is not duplicated by the work of the American abstractors to such an extent as to render it useless to include both publications in the index."

"It is found upon comparing the published list of the publications indexed by each set of abstracts as follows:—

Publications abstracted by the London Society ..	101
Publications abstracted by the American Society ..	516
Publications abstracted by the London Society not abstracted by the American	29

These 29 publications not covered by our American workers include the following, viz.:—German, 8; English, 12; Dutch, Swedish, and French, 2 each; and 1 each of Italian and Japanese.

"Comparing 6 pages of the English Society Index of 1909 with the corresponding American work of the same year it is found that out of 256 articles and monographs indexed by the English workers, 159 of these articles were not in any way referred to in the American Society Abstracts."

"These two facts together seem to fully answer the question, and show the necessity of including both works in the index."

May this criticism stimulate out American abstractors to greater zeal and accuracy, aside from the fact that many justified criticisms have been made that in some instances the abstracts are carelessly drawn up and give a very wrong idea of the originals.

Various difficulties were encountered in outlining a general plan for the index. If chemical bodies each had but one instead of several names, and if in chemical literature one never met with bodies as yet unnamed and therefore referred to by chemical formulæ only, then undoubtedly the dictionary plan pure and simple, with the names of the substances alphabetically arranged and the references to literature and patents collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use. Practically, however, most bodies known to chemists have a plurality of names, and the names approved and used in prior decades are generally not the names in highest repute nor in ordinary use to-day, nor is it at all sure that the names now in use will in most or even in many cases remain in use in years to come.

Where a chemical compound has several names (as indeed is usually the case) were it possible to decide now

(which perhaps might be done) which one of them is, on good scientific grounds, the most appropriate for index purposes in view of present knowledge, and further (which of course could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but while this might be done now in certain cases, which and how many of these names now used and approved will remain in use in years to come is something that no one can at present determine. Evidently the dictionary plan, unmodified, was not the best, and some better system had to be devised not open to these objections.

The system adopted was based on the chemical formula. In establishing for the Patent Office a card index to chemical literature, it was therefore decided to use, as an indexing basis, the kind and number of the component atoms of a chemical compound, these being its most unvarying characteristics, being subject only to errors of chemical analysis, and being therefore the most stable and unchanging basis for any scheme for the indexing and digesting of chemical literature; a conclusion reached at about the same time independently by Richter, as illustrated in his since published "Lexicon der Kohlenstoff-Verbindungen," and by other later workers in this field, the Patent Office system differing from that of Richter in being simpler and of more general application.

It was found that the simplest, most certain, and most direct system, was to re-write the so-called empirical chemical formula in a particular manner; that is to say, to write the atoms in the alphabetical order of their chemical symbols, upon library catalogue cards of standard size, and place these cards, arranged in alphabetical order, in standard library cases. For example, take the following chemical compounds:—

$(CH_3)_2C_2H_2(NO_2)_2$	Dinitrobutane
$(CH_3)_2CHNO_2$	Isopropylic nitrite
$KH_3C_2O_4$	Potassium acetate
CH_3Cl	Methyl chloride
$Cu(AsO_2)_2$	Copper arsenite

Re-writing them and arranging them alphabetically by formulæ instead of titles, they are:—

As_2CuO_4	Copper arsenite
CH_3Cl	Methyl chloride
$C_2H_3KO_4$	Potassium acetate
$C_3H_7NO_2$	Isopropylic nitrite
$C_4H_8N_2O_4$	Dinitrobutane

It should be noted, however, that the compounds containing carbon and hydrogen, and broadly included in the domain of organic chemistry, constitute so large and important a class that it is fully justifiable to depart slightly from the strictly alphabetical arrangement of chemical symbols, and write C always first and H accompanying C always second, in order to bring more closely together in the index bodies more or less closely related in chemical and physical properties.

In practice, therefore, the following general rule has been followed in compiling the chemical card index of the Patent Office:—Reject water of crystallisation and re-write the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds, C is to be written first and H second. Follow this re-written formula with the constitutional formula, when given, adding the water of crystallisation, if any, but arrange the cards alphabetically by the re-written formula.

The reason for disregarding water of crystallisation may be illustrated as follows:—The three bodies, Na_2SO_4 or anhydrous sodium sulphate, $Na_2SO_4+10H_2O$ or Glauber's salt, and the heptahydrated salt, $Na_2SO_4+7H_2O$, are in this way indexed under the same indexing formula, Na_2O_4S, and are thereby brought together, as they should be, for in solution they are chemically identical. If, on the other hand, water of crystallisation were taken into account for indexing purposes, the corresponding indexing formulæ would become Na_2O_4S, $H_{20}Na_2O_{14}S$, and $H_{14}Na_2O_{11}S$, respectively, and these three practically identical bodies would, in consequence, be widely separated in the index, which result would evidently be a very undesirable one.

The index was commenced and has been continued on the library-card catalogue plan, using the regular standard card, size $7\frac{1}{2}$ by $12\frac{1}{2}$ centimetres, or approximately 3 by 5 inches, without rulings except a single coloured horizontal line three-eighths of an inch below the top of the card—this for typewritten cards and cards upon which printed matter cut from books and periodicals is pasted. A limited use has also been made of cards having ruled lines, where for certain reasons the cards are written by hand.

I believe it would be very desirable to have an exchange of opinions on this subject in the correspondence column of this journal. It is our duty to assist by any helpful suggestions possible, the good work which is now being performed by the Washington Patent Office.—*Journal of Industrial and Engineering Chemistry*, v., No. 7.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

(Continued from p. 59).

III. *Electrodeposition of Tin by Separate Current* (continued).

10. Fearn recommends a bath which he prepared by dissolving 25 grms. of tartaric acid in about 400 cc. water, 75 gms. of caustic potash in about 400 cc. water, and 1·3 grm. of fused stannous chloride in 50 cc. of water. The caustic solution was added to the tin solution, then the tartaric acid solution mixed with it. Diluted to 1 litre, and electrolysed cold or hot. Thick bright deposit (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

11. Steele prepared an electro-tinning solution by dissolving 5·5 grms. of caustic potash, 16·5 grms. of potassium carbonate, and 66 grms. of sodium carbonate in 1 litre of water, after which he added 17·5 grms. of tin dioxide, 1 grm. potassium cyanide, and 1 grm. zinc acetate. Filtered before using (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249; Watt and Philip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345).

12. An alkaline bath proposed by Elsner for tinning iron and steel articles is prepared by putting 11 grms. of tin bichloride in 1 litre of water, then adding a solution of potash lye of 10° B. until the precipitate is dissolved, and 10 grms. of potassium cyanide (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 440).

13. Good deposits of tin may be produced by dissolving 1·5 grm. of fused stannous chloride, 80 grms. of potassium carbonate, and 1 grm. of potassium cyanide, separately in water; then adding the cyanide solution to the tin solution, and finally stirring in the carbonate solution. Dilute to 1 litre. This solution is not a very good conductor of current, thus requiring a high voltage; still satisfactory deposits may be obtained (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331).

14. Salzedes used a bath for tinning iron which he prepared by adding 10 grms. of potassium cyanide, 110 grms. of potassium carbonate, and 2·5 grms. of stannous chloride to 1 litre of water. By electrolysing with voltage at 4 to 5, a heavy dense deposit was rapidly obtained (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

15. An electrolyte patented by Fearn in 1873 contained

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii., No. 6.

1·2 grm. of fused tin bichloride, 111 grms. caustic potash, 111 grms. potassium cyanide, and 111 grms. of sodium pyrophosphate per litre. Each of these chemicals were separately dissolved in water; the tin solution was poured into the potash solution with constant stirring, then the cyanide solution was added, and finally the pyrophosphate solution. Electrolysed at ordinary temperature. Bright thick deposits were obtained. It was found necessary to add fused tin chloride to the bath from time to time, as the anodes were not dissolved as rapidly as the tin deposited (Watt and Philip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345; McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

16. The following solutions are capable of giving good white deposits upon all metals, and may be used cold:—

(*a*) Solution for electro-tinning brass, bronze, and copper; 7·5 grms. of caustic potash, 7·5 grms. of stannous chloride, and 35 grms. of potassium cyanide per litre.

(*b*) Solution for steel, wrought iron, and cast iron; 15 grms. of caustic potash, 15 grms. of stannous chloride, and 35 grms. of potassium cyanide per litre. Dissolve the caustic potash in water, add the tin chloride, then the potassium cyanide. If the tin chloride contains any iron, a precipitate will remain suspended in the solution, which should be filtered off. These solutions may be used either cold or hot. Better deposits are formed in the warm solutions. Use as large anode surface as possible, and electrolyse at tension of 2·5 to 3 volts (*Brass World*, 1911, vii., 121).

A more concentrated caustic solution than the above is said to have given very satisfactory deposits. It contained 60 grms. of soda lye, 45 grms. of fused stannous chloride, and 12 grms. of potassium cyanide per litre. Electrolysed at 1·5 volt (*Metal Industry*, 1907, v., 376).

17. J. C. Beneker obtained U.S. Patent 921,943, assigned to the Meaker Company of Chicago, for a tin electrolyte, the composition of which is 125 grms. of sodium hydroxide, 75 grms. of sodium thiosulphate, and 50 grms. of crystallised stannous chloride per litre. The solution is prepared by dissolving each of the salts separately, mixing the stannous chloride solution with the hydroxide solution, then adding the thiosulphate solution. It is stated that possibly the chief constituent of the prepared solution is sodium thiostannate (Na_2SnS). By using pure tin anodes, the deposit is produced without the formation of sponge or tree-like crystals, even when operated at high current density. The electrolyte may be used either cold or hot, but preferably hot (*Electrochemical and Metallurgical Industry*, 1909, viii., 285).

18. An electrolyte of composition similar to the Beneker solution contains 120 grms. of sodium hydroxide, 60 grms. of sodium hyposulphite, and 30 grms. of chloride of tin per litre (*Metal Industry*, 1911, ix., 90).

19. An electrolyte which is recommended to give excellent deposits of tin is prepared to contain 90 grms. of caustic soda, 15 grms. of sodium hyposulphite, 15 grms. of sodium chloride, and 30 grms. of tin chloride crystals per litre. This solution may be used either cold or hot, but gives better results when hot. Use anodes of pure tin (*Metal Industry*, 1910, viii., 87).

Conditions Necessary to Obtain Bright Dense Adherent Deposits of Tin.—The articles to be electroplated in any of these solutions must be carefully cleaned in a strong potash solution, then rubbed with lime, and subsequently thoroughly washed in clean water before placing them in the electrolyte. No time should be lost in getting the articles immersed in the plating solution directly after washing (McMillian Cooper, "Electrometallurgy," 1910 Ed., p. 249).

There is one drawback in depositing tin from most of the baths which are in general use, namely, the anodes are not dissolved in the same ratio as tin is deposited on the cathode, consequently the strength of the bath must be kept up by the addition of a tin salt. This is best accomplished by allowing a concentrated solution of the tin salt to drip constantly into the bath during the time it is working (Watt and Phillip, "Electroplating and Electrorefining," 1911 Ed., p. 342).

Tin baths should not be used at temperatures below 20° C.; as a general rule, the higher the temperature the better the deposit.

Too high current density causes a spongy deposit, which does not adhere; whereas, with a suitable current density, a dense reguline deposit will be obtained (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

W. Pfanhauser conducted a number of experiments of the formation of spongy and crystalline deposits of tin by electrolysis. He stated that the electroprecipitation of tin as thick adherent deposits is possible only in very concentrated tin-salt electrolytes, and those which contain no cations which will give rise to strongly dissociated solutions about the cathode. The best conditions for good tin deposits were found to be circulation of electrolyte, low current density, and high concentration of tin in the electrolyte. Spongy deposition is caused by poor circulation, dilute solutions, high current density, acid solutions, and impure solutions. Crystalline deposits form when the electrolyte contains no cations which are capable of forming alkali hydroxides or similar compounds, which are accompanied by the liberation of hydrogen. He used Roseleur's solution of tin chloride and sodium phosphate, and concentrated solutions of tin tetrachloride and stannous chloride (*Zeit. f. Electrochemie*, 1902, viii., 41; *Electrochemist and Metallurgist*, 1902, ii., 42; *Journ. Soc. Chem. Ind.*, 1902, xxi., 261).

In an article on "The Electrolytic Preparation of Tin Paste," the statement was made that "A spongy deposit may be due to various causes, but may be obtained nearly always by using too high a current density at the cathode. This results in an impoverishment of the electrolyte near the cathode with respect to the ions of the metal to be deposited, so that some other metal, and also generally hydrogen, is simultaneously deposited. It is under such conditions that the metal deposit becomes spongy (*Electrochemical and Metallurgical Industry*, 1905, iii., 59).

IV. *Electrolytic Refining of Tin.*

On account of the ease and comparative cheapness of refining tin by liquation methods (m.p. of tin = 232° C.) and by oxidation methods, electrolytic refining has little promise of being commercially employed.

Practically the only ore of tin is cassiterite (SnO_2; sp. gr. = 6·8 to 7·1; when pure it contains 78 per cent tin), which is found associated with such minerals as quartz, felspar, and mica in the form of granite or gneiss gangue. In some localities cassiterite is also accompanied by metalliferous minerals such as pyrite, arsenopyrite, chalcopyrite, wolframite, and molybdenite. These minerals, with the exception of wolframite, may be separated by water concentration methods. A recently developed method for separating wolframite, in case pyrite is also present, consists in calcining to the magnetic condition, then subjecting the pulverised ore to magnetic separation, the pyrite and the wolframite being removed (Schnabel-Louis, "Handbook of Metallurgy," II., 1907 Ed., p. 478; Louis, "Metallurgy of Tin," 1911 Ed., p. 12).

Commercial tin contains from 0·5 to 1·5 per cent of impurity, which is one or more of the following metals:—Zinc, iron, lead, bismuth, antimony, copper, arsenic, tungsten, molybdenum, silver. As there is no demand for very pure tin, and also because silver and gold are not present in quantity to pay for their recovery, electrolytic refining has, up to the present time, not been practised, except when very pure metal was wanted or when experimental refining was conducted. The product which is produced by pyro-heat methods of refining is of sufficient purity for commercial purposes.

A number of electrolytic methods have been developed, the majority using electrolytes of the stannous salt. The efficiency of the refining is given for some of the electrolytes, the figures being obtained by using the factors for stannous solutions which are 0·6163 mgrm. per coulomb,

2·2188 grms. per ampère-hour, 204·43 ampère-hours per pound; the factors for stannic solutions are 0·30817 mgrm. per coulomb, 1·1094 grm. per ampère-hour, 408·86 ampère-hours per pound.

1. Brand conducted experiments on the electrolytic refining of tin, using an electrolyte containing 2·5 per cent by volume of concentrated hydrochloric acid and 9 per cent by weight of stannous chloride. The method did not find commercial application (Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II., p. 549; Dammer, *Chem. Technology*, ii., 27, 324).

2. Michaud and Delasson received French Patent 435,936 for the use of a tin electrolyte prepared by dissolving stannous chloride in water, adding sulphuric acid till the precipitated oxychloride dissolved, and then stirring into the solution about 1 per cent of magnesium chloride and 1 per cent of boric acid. The cell used for the refining is constructed with a sheet copper cathode placed horizontally on the bottom, on which the tin crystals are deposited and removed by scrapers (*Journ. Soc. Chem. Ind.*, 1912, xxxi., 395).

3. Mennicke conducted experiments on the electrolytic refining of tin in fluosilicate electrolytes, and obtained deposits which were similar to lead deposits produced under the same conditions of current-density and temperature. The electrolyte was prepared by dissolving freshly precipitated stannous hydroxide in hydrofluosilicic acid in proper proportions to give a solution containing 10 per cent free hydrofluosilicic acid by weight. Tin oxide was found to be insoluble in hydrofluosilic acid. The presence of free hydrofluoric acid was found not to interfere with the production of satisfactory deposits.

The electrolysis was conducted at 20° C., using current at density of 9·3 ampère per sq. ft. (1 amp. per sq. dm.) and an average of 0·4 volt. Distance between electrodes about 2 inches (5 cm.). The tin deposited extremely solid and tough, even without the presence of any addition-agent such as gelatin or albumen. The lower the voltage the finer the crystals.

Better results were obtained by using pure tin anodes than with those of a tin alloy. The presence of lead finally caused the deposit to become spongy, but still the deposited tin was pure. He states that very pure tin can be produced, which is especially suited for preparing pure chemicals (*Electrochem. Zeit.*, 1905, cxii., 135, 161, and 180; *Zeit. f. Electro. Chem.*, xii., 112; *Electrochem. and Metallurgical Ind.*, iv., 26; *Mineral Industry*, xiv., 555; Betts, "Lead Refining by Electrolysis," 1908, p. 47).

4. Mention has been made that neutral concentrated solutions of either stannic chloride or stannous chloride can be used for producing pure tin, as these electrolytes yield a coarse crystalline deposit (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 148).

5. Beautiful dense deposits of tin can be produced without the evolution of hydrogen at the cathode by electrolysing a solution of sodium-stannous chloride with low current-density and at ordinary temperature (*Bull. Soc. d'Enc. L'Ind. Nat.*, July, 1912, p. 28).

6. Quintane was granted English Patent 5496 for the deposition of pure tin by use of an electrolyte composed of stannic chloride, or stannous chloride, and an ammoniacal salt, preferably ammonium chloride. It is claimed that a perfect deposit of chemically pure tin was produced from this solution. The statement is made that "to obtain a clear solution, and one that will act as a good conductor of the current, the precipitate first formed on dissolving the tin salt in water is re-dissolved by the addition of ammonium chloride, and the solution filtered. The current should be weaker than that employed for the electro-deposition of copper, or the deposit will be irregular" (*Journ. Soc. Chem. Ind.*, 1900, xix., 1121; *Mineral Ind.*, ix., 646).

7. Hollard prevented the formation of spongy deposits of tin by using an electrolyte composed of 12 grms. of sodium stannate (Na_2SnO_3) and 200 grms. of sodium sulphate per litre, and electrolysing it at a temperature of 80° C. at current-density of 2 ampères per sq. ft. (0·2 amp. per sq. dm.) (*Bull. Soc. d'Enc. Ind. Nat.*, July, 1912, p. 28).

8. Fischer satisfactorily deposited tin by using a solution of ammonium sulpho-stannate to which was added a reducing agent such as sodium sulphite, sodium hyposulphite, or potassium cyanide (*Zeit. Anorg. Chem.*, 1904, xlii., 363).

9. Neumann received German Patent 198,289 for a process of obtaining pure dense deposits of tin by use of an electrolyte composed of an alkali sulpho-stannate, and operating at temperature of about 70° C. The presence of free alkali is said to be advantageous.

10. Claus refined tin in an aqueous solution of sodium sulpho-stannate, of sp. gr. 1·07, and at 90° C., employing current at 10 ampères per sq. ft. (0·9 amp. per sq. dm.). All the impurities except arsenic and antimony collected as anode sludge, principally as sulphides. Arsenic and antimony, when present, were precipitated on the cathode with the tin. He found that the cathode tin containing arsenic and antimony could be freed from these by making it an anode in an acid solution of sodium thiosulphate containing hydrochloric acid, the arsenic and antimony in this case remaining as sulphides in the anode sludge. The cathode tin was melted and cast into bars (*Electrochem. Zeit.*, viii., 168; Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., xi., 549).

11. Patents have been granted to O. Steiner for a tin refining process, using an electrolyte similar to that published by Claus, as given above (10). The patents issued are:—U.S. Patent 890,249; German Patent 193,528; English Patent 10,230; French Patent 374,116. The claims are that by using an electrolyte containing about 10 per cent by weight of an alkali sulphide, to which has been added about 1 per cent by weight of flowers of sulphur, tin of high purity (99·9 per cent) could be produced as a dense smooth deposit, when the electrolysis is conducted so that the E.M.F. is kept below 0 2 volt, current-density under 4·5 ampères per sq. ft., and solution kept at about 90° C.

The electrolyte is prepared by dissolving commercial sodium sulphide in the necessary amount of water to produce a 10 per cent solution, adding 1 per cent by weight of flowers of sulphur, letting settle, then filtering. It is necessary to analyse the solution at intervals during the electrolysis, and to add sodium sulphide and flowers of sulphur so as to keep up the concentration. The loss of sodium sulphide will be due to oxidation and to the formation of sodium sulpho stannate. The amount of tin in the electrolyte reaches a maximum of about 2·2 per cent by weight, and remains constant thereafter so long as the concentration of sodium sulphide is kept proper.

One of the essentials in the use of this solution for refining tin is that the voltage must be kept below 0·2, and that the electrolyte be maintained above 90° C. If the potential is allowed to rise, gassing at the cathode occurs. At 0·6 volt violent liberation of hydrogen takes place, with decomposition of the electrolyte, and at the same time the tin deposits as a dull spongy mass which contains oxide.

The raw tin should not contain more than 10 per cent of impurities, and the iron content should be below 2 per cent, otherwise the anode sludge will adhere and cause the voltage to rise and produce gassing and a spongy deposit. The anode sludge will contain the iron, lead, antimony, copper, bismuth, and silver. Distance between the electrodes about 1½ in. (3·5 cm.). Iron tanks are most suitable.

The conditions which are given as being necessary to obtain high current efficiency and to produce dense pure deposits are:—

(*a*) Temperature of electrolyte above 90° C.

(*b*) Thorough and constant circulation, or mixing of electrolyte.

(*c*) Voltage maintained below 0·2.

(*d*) Pure plate cathodes (cathodes of iron, copper, and lead cause the voltage to rise and the deposit to be non-adherent and spongy).

(*e*) Pure electrolytes, free of arsenic, antimony, copper, &c.

(*f*) Electrolyte containing 10 or more per cent of sodium sulphide by weight. A more concentrated solution permits the use of higher current-density.

(*g*) Add to the electrolyte about 1 per cent by weight of flowers of sulphur just before placing a new lot of anodes in the tank. The sulphur is necessary to form sulphides with the impurities in the anode, thereby preventing the contamination of the electrolyte.

(*h*) The electrolysis must not be interrupted until the anodes are to be removed. When the current is interrupted, gassing will occur when the current is switched on, and spongy deposit will form.

A means of maintaining the same current-density from a number of electrodes when placed in the same tank, was accomplished by soldering all of the anodes to the same supply conductor and all of the cathodes to the negative conductor. When this was not done the voltage between all of the opposite electrodes was not the same.

The ampère-hour efficiency is given as above, 98·5 per cent. It is also stated that "the deposit could be still improved by adding a colloid to the electrolyte, for example, gelatin as is used in the Betts' process for electrolytically refining lead" (*Electrochem. Zeit.*, May, 1908; *Journ. Soc. Chem. Ind.*, 1907, xxvi., 768; *Electrochem. and Metallurgical Ind.*, 1907, v., 309).

12. Sperry obtained U.S. Patent 874,707 for a process of refining tin by the use of a diaphragm cell. It is stated that electrolytes consisting either of sulphate, ammonium oxalate, ammonium sulphide, or of chloride, fluoride, or hydrofluoric acid could be used in the cell. The impure metal to be electrolytically refined may be given a preliminary refining by fire-methods in order to remove the major portion of the impurities, then cast into anodes. The use of the diaphragm between the anodes and the cathodes is to prevent the cathode deposit becoming contaminated by floating anode sludge. The impurities which accumulate in the electrolyte as soluble salts are to be removed periodically by withdrawal of a portion of the electrolyte, and replacing it by fresh solution. Electrolytes work better when kept at 85° C. (*Journ. Soc. Chem. Ind.*, xxvii., 343; *Electrochem. and Metallurgical Ind.*, vi., 76).

There are several articles, in themselves reviews, which could not be reviewed. They may be found in the following publications:—

Electrical Engineering, London, July 15, 1898, "The Electrolytic Refining of Tin and Recovery of Tin from its Ores," by Sherard Cowper-Coles.

Electrochem. Zeit., Berlin, March, 1907, "Recent Progress in the Metallurgy of Tin, with Regard to Electrochemistry in 1906," by H. Mennicke.

Electrochem. Zeit., Berlin, July, 1908, "Progress in the Metallurgy of Tin with Special Reference to Electrochemistry in 1907," by H. Mennicke.

Electrochem. Zeit., Berlin, January, 1910, "Electrolytic Precipitation of Tin," by B. Pasztor.

(To be continued).

NOTICES OF BOOKS.

A Text-book on Trade Waste Waters: Their Nature and Disposal. By H. Maclean Wilson, M.D., B.Sc., and H. T. Calvert, M.Sc., Ph.D., F.I.C. London: Charles Griffin and Co., Ltd. 1913.

In this book the nature and disposal of the waste liquids of the important industries are discussed in great detail. The coal trade, gas manufacture, brewing, leather, paper, and textile trades are considered in turn, the latter being given specially full treatment, and in each case the most important practical methods of treating the liquid refuse are described, with plans and diagrams of the necessary plant and full statistics as to cost of working and efficiency. The advice given to manufacturers regarding choice of methods, the necessity for constant analyses and for the correct estimation of the volume of the refuse is always thoroughly practical, and the results of many years of experience of the working of the Rivers Pollution Prevention Acts are embodied in the book. An excellent outline of the methods usually employed in the analysis of waste waters is included.

Jahrbuch der Elektrochemie und Angewandten Physikalischen Chemie. Berichte uber die Fortschritte des Jahres 1906. ("Year Book of Electrochemistry and Applied Physical Chemistry. Reports of Advances in the Year 1906." Edited by Dr. phil. Heinrich Danneel and Prof. Dr. Julius Meyer. Vol. XIII. Halle (Saale): Wilhelm Knapp. 1913. (M. 32).

This year-book is divided into two sections, the first and longer of which treats of the developments of the scientific side of the subject, while in the second part the applications of electrochemistry are considered. The treatment is very comprehensive and thoroughly systematic; no very important discoveries have to be recorded, but, on the other hand, general advances have been made in all branches. It is greatly to be regretted that it has not been found possible to issue Volume XIII. of the year-book somewhat earlier; in the last seven years the growth of the subject has been rapid, and much that was published in 1906 must now be regarded as out of date.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 21, May 26, 1913.

Action of Ammonia on Monoethylamine.—Félix Bidet.—The author has already shown that the action of ammonia on the hydrochlorides of amylamine and ethylene diamine constitutes a chemical equilibrium. The study of the action of the gas upon solid anhydrous monoethylamine hydrochloride shows that the velocity of the reaction is greater than with the other hydrochlorides. It decreases appreciably as the pressure of the ammonia diminishes. The velocity is greater for the inverse than for the direct reaction.

Instability of Ferric Fluosilicate.—A. Recoura.—Berzelius stated that ferric fluosilicate could be obtained as a gummy semi-transparent mass by saturating fluosilic acid with ferric hydrate and evaporating the solution. The author's experiments prove, however, that ferric fluosilicate does not exist, and when attempts are made to prepare it either by Berzelius's method or by double decomposition it immediately splits up into another more stable double fluoride, losing one-third of its silicon fluoride, $(SiF_4)_3Fe_2F_6 = SiF_4 + (SiF_4)_2.Fe_2F_6$.

Ether Salts Derived from Octanol-2.—J. B. Senderens and J. Aboulenc.—By keeping a mixture of octanol-2 (one molecule) and organic acid (1·05 mol.) at a temperature not exceeding 100° ether salts can be obtained, if 2 to 3 per cent of H_2SO_4 is added as a catalyst. Sulphuric acid does not act as a catalyst towards those aromatic acids in which the carboxyl is directly united to the radicle, but if the carboxyl is separated by a chain, as in phenylacetic acid, it brings about catalytic etherification.

Condensation of Primary and Secondary Aromatic Amines with Mesoxalic Ethers.—A. Guyot and J. Martinet.—The condensation of primary amines, such as monoethylaniline with ethyl mesoxalate, is readily effected,

the principal product being a dioxindol-3-carbonic ether, while a small quantity of phenyl tartronic ether is also formed. The former ether is readily saponified by means of aqueous potash, the corresponding dioxindol being obtained. The saponification has to be carried out in absence of air, otherwise the alkaline solution absorbs oxygen and the dioxindol is transformed quantitatively into isatine.

Action of α-Monochlorhydrine and Epichlorhydrine upon Monosodium Glycerin.—Jean Nivière.—When monosodium glycerin reacts on α-monochlorhydrine glycide is the principal product, some diglyceric alcohol being also obtained. With epichlorhydrine a polymer of the anhydride of diglyceric alcohol is formed. It is a white amorphous substance insoluble in water, alcohol, ether, pyridine, and nitrobenzene. When boiled with acetic anhydride in presence of fused sodium acetate it gives a diacetyl derivative. Both substances decompose when heated without undergoing decomposition.

Properties of Carbon Tetraiodide and its Estimation in presence of Iodoform.—Marcel Lantenois.—Tetraiodide of carbon is decomposed quantitatively even in the dark by pure oxygen, iodine being liberated and carbon oxyiodide formed. The oxyiodide is unstable, and the gases formed during the reaction also contain carbon monoxide and a small proportion of carbon dioxide. The action is facilitated by light. In atmospheric air the transformation is less rapid. Carbon iodide reacts with a certain number of metalloidal chlorine compounds to give the corresponding iodide and a chloroiodide of carbon. When carbon iodide reacts with silver nitrate the two following equations appear to take place simultaneously :—

$$CI_4 + 4AgNO_3 + 2H_2O = CO_2 + 4HNO_3 + 4AgI,$$
$$3CI_4 + 12AgNO_3 + 6H_2O = 3CO + AgIO_3 + 11AgI + 12HNO_3.$$

Each of these reactions gives a molecule of gas for a molecule of tetraiodide. Hence whatever the proportions of the two oxides of carbon the volume of their mixture bears a definite relation to the weight of iodide. This reaction can be applied to estimate the tetraiodide in presence of iodoform. The volume of gas obtained is 42·9 cc. for 1 grm. of tetraiodide, and 56·6 cc. for 1 grm. of iodoform, and the two gases can be measured with great accuracy.

MISCELLANEOUS.

City and Guilds of London Institute.—On the report of the Delegacy of the City and Guilds (Engineering) College, the Council of the City and Guilds of London Institute have awarded the Diploma of "Associate of the Institute" to the following matriculated third year students who have completed a full course of instruction as prescribed by the Council. (An asterisk denotes entered as a second-year student):—*Civil and Mechanical Engineering* (57 out of 90)—O. B. Binns* (Bramwell Medal), W. H. Thomas (Henrici Medal), A. Singh Sarkaria, W. Collins, G. L. Groves, A. E. Walker, F. G. D. Stoney, E. Robinson,* F. J. G. Foot, C. W. J. Taffs,* F. White,* F. Buckingham,* Q. Z. Huzain, E. S. May, Anokh Singh,* W. R. Sheffield, J. W. Bansall,* J. T. Down, J. M. Boyd, I. Edeleanu, R. H. Paddison, K. L. Nanda, A. M. R. Montagu,* J. N. Nanda, H. W. L. Poole, S. E. M. Firth, L. A. Ritchie, J. A. Mercer,* E. L. Wildy, W. M. Carmichael, F. H. Hutchinson, C. T. W. Sauerbeck, P. V. Hoare,* J. H. Fletcher, E. F. Elderton, M. D. Willcock,* K. Singh, M. Fatehullah, S. P. Hannam, D. Milner,* E. Ramirez, G. E. Gill, J. S. Roberts, F. R. Roberts, J. H. Saint, P. R. Purves, L. L. Vigers, E. G. Timbrell,* R. G. Cleveland, J. D. Davies, H. D. D. Smith, F. L. Richards, C. G. Whitmore,* E. A. P. Wood, O. Hodgson,* F. D. Napier-Clavering, G. C. Totton. *Electrical Engineering* (21 out of 27)—E. A. Richards (Siemens Memorial Medal), R. S. H. Boulding* (Siemens Memorial Medal), D. Dunham, G. J. Websdale, D. H. Linsley, N. H. Barker,* U. Singh, L. B. Hobgen, L. G. Floyd, H. B. Lee, A. G. C. Holroyde, V. H. G. Parker, J. C. Elmer,* R. C. Wrinch, J. P. Clifton, H. A. Denison, W. Ryley, N. D. Edingborough, A. H. Hall, P. Jackson,* H. Singh Siddhù. *Chemistry* (6 out of 8)—A. W. Long, E. Watson, C. E. M. Richards, D. W. C. West,* N. J. Read, K. Hooper.

University of London.—*Appointments Board.*—The Appointments Board, constituted by the Senate to assist Graduates and Students of the University in obtaining appointments, and to co-ordinate and supplement the work done by the Schools and Institutions of the University in this direction, registers the qualifications of: (*a*) Graduates of the University of London; (*b*) Graduates of other Universities who are students of London; (*c*) Undergraduates in their last term, previous to entry on Degree Examinations. The fee for registration has for the present been fixed at 5s., renewable annually so long as the name is retained on the registers. The Board reported to the Senate in June, that since the appointment of a full-time Secretary the work of the Board had increased to a very considerable extent. The Secretary had visited permanent officials of many Government Departments, and received promises of support in the work of the Board; he had also visited the officials of the Oxford and Cambridge Appointments Board, the Teachers' Registration Council, and a number of Principals, Headmasters, Headmistresses, and Secretaries of Educational Organisations. The London Chamber of Commerce, the Association of University Women Teachers, the Central Bureau for the Employment of Women, and various Colleges and Schools had expressed their readiness and desire to co-operate with the Board. Upwards of 200 graduates and stedents had visited the Secretary—many to seek specific advice. The Secretary (Dr. A. D. Denning) will be pleased to give further information, and to see graduates at the Central Offices of the University, South Kensington (Room 23) on Wednesday afternoons, 2 to 5, or Thursdays, 12 to 1.30, or at other times by arrangement. Educational Authorities, Business Firms, and others, having openings for Graduates, are asked to inform the Secretary, who will forthwith notify the more suitable available Graduates on his registers, and use every endeavour to secure the candidature of the most capable applicants. Approximately 1000 posts have been notified to suitably qualified graduates registered with the Board within the last three months and many appointments secured. Further registrations of well-qualified graduates and students are now necessary.

Uses of Cast Silicon.—According to *Metallurgical and Chemical Engineering*, xi., 103, silicon is used in the form of pipes for the conveyance of acid gases at a high temperature from stills to condensers, also in the construction of the condensing batteries themselves, proving more efficient than stoneware owing to its high thermal conductivity and ability to withstand sudden changes of temperature. Silicon pipes are also used for the transportation of hot liquid sulphuric and nitric acids, but it cannot be used for hydrochloric acid unless the discoloration resulting from the slight solubility is immaterial. It is used as a lining in centrifugal pumps, acid valves, and pipes for the elevation of corrosive liquids by compressed air, and for the construction of ploughs in ore roasters it is said to have proven efficient. Cast silicon is also being employed in the form of shallow pans and pots for the concentration of zinc chloride solutions, supplanting the enamelled stoneware vessels which are rapidly destroyed. Cast silicon ware is said to be produced in practically all shapes required by the chemical industries, such as, for example, pipes, evaporating vessels, receivers, tiles, alembics, crucibles, and pump parts.—*Journal of Industrial and Engineering Chemistry*, v., No. 3.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2803.

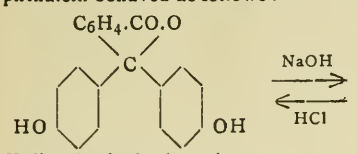
CRITICISM OF A RECENT CONTRIBUTION TO THE THEORY OF INDICATORS.

By ARTHUR G. A. MILLER. B.Sc. (Lond.), F.C.S.

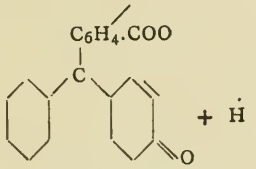
In a recent contribution to the theory of indicators (Dr. J. Waddell, Chemical News, 1913, cvii., 206), the author states that, according to the ordinary theory of indicators, it is strange that methyl-orange, a strong acid, should act towards weak acids, as phenolphthalein, a weak acid, acts towards weak bases, and that the anomaly is removed if methyl-orange is considered to be a weak base instead of a strong acid.

The author appears to have based his conclusion upon purely physico chemical considerations, without having due regard to the question of the chemical constitution of the indicator, which is now generally admitted to play a most important part. Indeed, many chemists are strongly of the opinion that the two views are complementary, and experimental evidence seems to confirm this. Indicators are now regarded, not as a true, but as *pseudo* acids or bases (so-called by Hantzsch), and that the undissociated molecule is really a mixture of one or more tautomeric forms in equilibrium, only one of which ionises to a considerable extent (see H. T. Tizard, *B.A. Reports*, 1911, p. 268).

Thus, on the old theory, it was considered that phenolphthalein behaved as follows :—

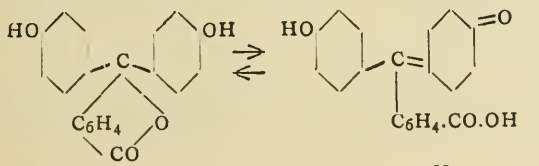


Undissociated colourless substance (lactone).



Coloured quinonoid ion.

At the present time it is considered as showing the following equilibrium in solution :—



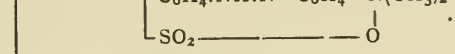
Coloured ion.

Configuration I. is the more stable, and the acid is very weak; hence, Configuration II. and its ions are only present to a very small extent in the solution, which in consequence is colourless. Addition of bases (hydroxyl ions) diminishes the concentration of hydrogen ions to such an extent that the colour due to Configuration II. makes its appearance. Consider the case quoted by the author, of the removal of the colour produced by the action of concentrated ammonia solution on phenolphthalein, by the addition of ammonium salts such as ammonium chloride. As is well known, ammonia solution contains hydroxyl ions in relatively small amount. Applying the law of mass action, any addition of ammonium salts (ammonium ions) must diminish the concentration of hydroxyl ions in order to preserve equilibrium, and with corresponding increase of hydrogen ion concentration Configuration I. becomes the stable one; that is, the solution becomes colourless. Chemical evidence is not lacking in support of the statement that tautomerism exists. In the case of phenolphthalein the red colour is destroyed on the addition of alcohol or acetone, and this is undoubtedly due to ionisation change. On the other hand, the dry salts of the indicator are red, and, further, a coloured quinonoïd carboxylic methyl ester has been isolated; in these cases there can be clearly no question of ionisation. Both explanations are thus accounted for in dealing with the colour change of phenolphthalein.

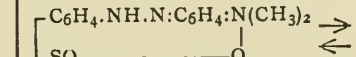
Coming now to the case of an amphoteric indicator (*i.e.*, one which has both acidic and basic groupings in the molecule) such as methyl-orange, its sodium salt,—

$$NaSO_3C_6H_4N=NC_6H_4N(CH_3)_2,$$

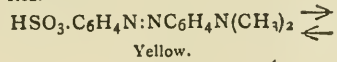
is yellow, while the free acid is violet. It seemed very probable that the strongly acidic sulphonic group was modified by the basic aminic group, and accordingly Hewitt (*Analyst*, 1908, xxxiii., 85) assigned to the free acid in the solid condition, or in acid solution, the constitution of an internal salt. Thus,—



This view was put forward about the same time independently by Hantzsch (*Ber.*, 1908, xli., 1187). Thus the aqueous solution consists of an equilibrium mixture of the internal salt, the true dimethylaminoazobenzene sulphonic acid, and the ions of the latter :—



Red.



Yellow.

Yellow.

Addition of hydrogen ions will diminish the dissociation and produce the internal quinonoïd configuration, while, on the other hand, the addition of even a weak base will remove hydrogen ions, and the yellow colour due to the azoïd ions will appear. There is, again, chemical evidence for the assumption that tautomerism exists in this case. Thus the sodium salt of methyl-orange has the well-known orange-yellow colour, and it has been shown that the dry silver salt has the same violet colour as the free "acid." Clearly here there is no case of ionic dissociation, and it is naturally concluded that the free acid of methyl-orange can exist in tautomeric forms.

One has now to explain the behaviour of methyl orange to a weak acid such as acetic acid. Consider an indicator which is a weak acid (methyl orange is relatively weak in comparison with a strong mineral acid), and let its degree of ionisation in solution be α. Appling Ostwald's law of dilution one has—

K × concentration of undissociated molecules = concentration of dissociated molecules × concentration of hydrogen ions,

or—

$$K \times \frac{1-\alpha}{\alpha} = \text{concentration of hydrogen ions};$$

where K is the dissociation constant of the indicator. The degree of ionisation of an indicator, and therefore of its colour, thus depends upon the constant K and the concentration of hydrogen ions in the solution. Thus for every indicator there is a particular concentration of hydrogen ions necessary to produce a colour change (see Salm, *Zeit. Phys. Chem.*, 1906, lvii., 471). For methyl-orange the concentration of hydrogen ions lies between 10^{-3} and 10^{-4} normal. Evidently there is such a concentration of hydrogen ions present in a weak acid like acetic acid, but it is very easily diminished by the addition of acetone, alcohol, or acetates, so that the now unstable red internal quinonoïd configuration gives place to the stable tautomeric azoïd form, which at once ionises with the production of the well-known yellow ion.

Dr. Waddell points out that the sulphonic group is strongly acidic, but acting against this is the aminic group, conferring a basic character which is accentuated in the sodium compound. There is, however, no doubt that the acidic character of the molecule predominates. At the same time, it is believed that the basic character of the aminic group very largely influences the sensitiveness of the indicator to hydrogen ions. Thus dimethyl-α-naphthylamine is more basic in character than dimethylaniline, and the author of this communication found that an indicator prepared by coupling the former substance with diazotised sulphanilic acid was more sensitive to hydrogen ions than methyl-orange. On the other hand, diphenylamine is almost non-basic in character, and the azo-compound made by coupling it with diazotised sulphanilic acid was found to require a considerable concentration of hydrogen ions to effect a noticeable colour change.

Finally, Dr. Waddell stated that he believed if almost dry hydrochloric acid was passed into an alcoholic solution of methyl orange the colour of the solution would still remain yellow. The experiment has been carried out using a solution of methyl-orange in absolute alcohol, but there was an immediate red coloration produced owing to the fact that hydrochloric acid, one of the strongest acids, can exert its power of ionisation even in the presence of absolute alcohol.

Thus it seems as if the theory of indicators accepted at the present time is in complete accord with the behaviour of methyl-orange, and that Dr. Waddell's views regarding the yellow sodium salt of methyl-orange as being undissociated in solution, and the red colour produced by the addition of acids is due to the dissociated cation are untenable.

Chemical Laboratory.
Education Department, George Williams' College,
London Central Y.M.C.A.

PRELIMINARY NOTE ON A NEW METHOD FOR THE DIRECT DETERMINATION OF RUBBER.*

By L. G. WESSON.

The chief difficulty that has stood in the way of the direct determination of rubber has been the uncertain composition of the derivatives, such as the tetrabromide and nitro compounds, used in the methods proposed up to date. This has suggested a method which avoids this source of error by forming a derivative, the nitrosite, whose composition is immaterial so long as it contains all the carbon which belonged to the rubber of the sample under analysis. On analysing this derivative for carbon, we are then enabled to calculate how much rubber the derivative represents.

The procedure, in brief, consists in allowing the acetone-extracted sample to dissolve or swell up in carbon tetrachloride, after which nitrous gases, evolved by dropping HNO_3 on As_2O_3, form the nitrosite of rubber by passing through the solution to saturation. After standing, the now soluble nitrosite is dissolved in acetone, from which it is obtained in a form ready for combustion by a method of precipitation or evaporation. The details of both of these methods are being studied to eliminate known sources of error and to further simplify the manipulation.

The tediousness of the latter has been considerably relieved by the development of a durable electric organic combustion furnace adapted for this work. It consists of a tube of Jena glass 60 cm. long and 2½ cm. bore, containing a coil of electrically heated platinum wire, and a boat of lead peroxide and minium heated by an external coil of nichrome wire. Two heavy copper wires, coated with iridium and pushed through the one-holed rubber stopper at the forward end of the tube, solve, in a convenient manner, the problem of making an external contact for the useful directly heated catalyser coil. The leads for the coil simply rest on the hooked ends of these wires, thus permitting an easy removal and replacement of the stopper, the coil, or the lead peroxide boat which rests between the coil and the stopper. It is thought that, with a few modifications, this form of furnace is adapted for general organic combustions, and it will be tested soon with that end in view.

The use of the lead peroxide boat which absorbs the sulphur of the nitrosite as lead sulphate, should give a means for the estimation of the sulphur of vulcanisation, if, as Alexander emphatically asserts (*Ber.*, xl., 1077; *Zeit. Angew. Chem.*, xx., 1364; xxiv., 687), the sulphur combined with the rubber is carried quantitatively into its nitrosite.

The following figures have been obtained by the use of either the precipitation or evaporation methods:—

A washed and dried fine para, precipitated once from chloroform, dried to constant weight in hydrogen at 92°, and analysed as 99·1 per cent carbon plus hydrogen, gave 99·5, 98·7, 97·8, 98·0, 97·1, and 96·6 per cent $C_{10}H_{16}$.

A washed and dried fine para gave 95·7, 94·7, 94·8, 95·2, and 95·5 per cent $C_{10}H_{16}$.

A rubber compound containing litharge, whiting, barytes, zinc oxide, sulphur, and 48 per cent para, or 45·4 per cent rubber, gave 45·3, 46·4, 48·7, 47·2, and 45·6 per cent $C_{10}H_{16}$.

Another containing the same ingredients with the addition of paraffin, with 28·6 per cent fine para or 27·8 per cent rubber, gave 27·5, 27·4, 27·7, 26·7, 27·1, and 26·9 per cent $C_{10}H_{16}$.

These results, however, represent only those that have been obtained under the best conditions, and are not subject to the numerous sources of error that have continually appeared. They seem to be of sufficient value to justify putting on record at this time. Further work should give a greater reliability and accuracy, in which case full details of the method and apparatus will be published.

* Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913. (Published by permission of the Director of the Bureau of Standards). From *Journal of Industrial and Engineering Chemistry*, v., No. 5.

POTASSIUM PERMANGANATE IN THE QUANTITATIVE ESTIMATION OF SOME ORGANIC COMPOUNDS.*

By C. M. PENCE.

Potassium permanganate has been most generally used in the volumetric estimation of iron. Some uncertainties formerly existed since it was impossible to obtain a chemically pure article, and insufficient data were at hand as to proper methods of preparation and standardisation of its solutions.

At present these objections have been largely overcome, and almost all of our text-books on quantitative analysis contain an extended treatise on proper means of preparation and standardisation of volumetric permanganate solutions.

* Read before the Indiana Section of the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, v., No. 3.

One of the most commonly known organic compounds that is quantitatively determined by the use of volumetric permanganate is oxalic acid. Now oxalic acid and iron are determined in acid solution, but the procedure most applicable for the oxidation of all types of aromatic compounds as well as carbobydrates and hydrocarbons is with alkaline permanganate. Oxidations in acid solution are less energetic than those with alkaline $KMnO_4$, and in the latter case the final product of a completed decomposition of the organic compound is oxalic acid instead of CO_2 and H_2O.

Among the substances mentioned in the literature (see Note) as being oxidised to oxalic acid are propylene, isobutylene, amylene, acetone, fatty acids; butyric, lactic, succinic, and tartaric acids; dextrose, sucrose, glycerol, and phenol. Now when an organic compound is oxidised to oxalic acid, a further oxidation to CO_2 and H_2O readily follows upon acidifying and warming the solution. Such a procedure forms the nucleus of a method for the determination of the compounds previously enumerated. Tocher made use of this method, and found that phenol could be determined. His method was substantially as follows:—Dissolve 1 grm. phenol in 1000 cc. distilled water, and take 10 cc. for titration. Add 3 to 4 grms. $NaHCO_3$ together with a little distilled water. Then add 50 cc. $KMnO_4$, and boil for five minutes. Set aside to cool, and gradually add dilute H_2SO_4 to decided excess; warm to 60° C., and titrate the excess of N/10 $KMnO_4$ with N/10 oxalic acid.

(Note. — "Oxidation of organic Compounds with Alkaline Permanganate," Eduard Donath and Hugo Ditz, *Journ. Prakt. Chem.*, 1899, [2], lx., 566; through *Journ. Chem. Soc.*, 1900, [1], lxxviii., 197; "Contribution to the Knowledge and Determination of the Carbohydrates," J. König, W. Greifenhagen, and A. Scholl, *Zeit. Nahr. Genussm.*, xxii., 705; through Abstr. *Journ. Am. Chem. Soc.*, 1912, vi., 901; "Volumetric Determination of Phenol," Jas. F. Tocher, *Pharm. Journ.*, lxvi., 360).

This method was found to be open to the following objection:—That the manganese dioxide formed as a result of the action of N/10 $KMnO_4$ upon the phenol did not reduce readily enough with consequent solution upon direct titration with N/10 oxalic acid. Thus the solution was full of oxide which not only obscured but rendered the end-point of little value, in that the oxide was not completely reduced before the permanganate end-point was obtained.

The following modification of Tocher's method was found to give good results:—

Dissolve 0·4 grm. phenol in 1000 cc. distilled water. Place 50 cc. N/10 $KMnO_4$ and 3 to 4 grms. $NaHCO_3$ in a 500 cc. glass-stoppered Erlenmeyer flask. Add 25 cc. of the phenol solution with gentle rotation. Boil five to ten minutes (with stopper removed). Cool flask to about 60° C. Acidify with dilute H_2SO_4, let stand about two minutes; cool to room temperature. Dilute with distilled water, add 5 cc. 20 per cent KI, and titrate the liberated iodine with N/10 thiosulphate solution, using starch as indicator. The number of cc. of N/10 thiosulphate subtracted from the number of cc. $KMnO_4$ originally added = No. cc. of $KMnO_4$ consumed by the phenol.

1 cc. N/10 $KMnO_4$ = 0·000336 grm. phenol.

If a glass-stoppered Erlenmeyer flask is not available an ordinary Erlenmeyer may be used, and its contents transferred to a glass-stoppered bottle before acidifying. Any oxide adhering to the Erlenmeyer is easily removed by the addition of a little distilled water acidified with H_2SO_4, and containing a few drops of 20 per cent KI.

In considering the nature of the oxidation with $KMnO_4$ in acid and alkaline solutions it is observed that each molecule of $KMnO_4$ in acid solution liberates 2·5 atoms of oxygen according to the following equation:—

$$2KMnO_4 = K_2O + 2MnO + 5O,$$

or—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Now in alkaline solutions the two molecules of MnO are immediately oxidised to $2MnO_2$ at the expense of 2 atoms of oxygen, so that we actually have $2KMnO_4 = K_2O + 2MnO_2 + 3O$. Hence, for each molecule of $KMnO_4$ used, only 1½ atoms of oxygen are available for our oxidation process. This fact must be recognised in providing sufficient $KMnO_4$ to readily complete the oxidation process, and it would necessarily enter into a calculation of the value of N/10 $KMnO_4$ in terms of phenol if the MnO_2, or rather its hydrated form, were filtered from the solution before acidifying and adding the KI. But since the procedure is not lengthened by a filtration the MnO_2 is reduced to its manganous form with the liberation of free iodine, and we must calculate our factor by considering that reaction proceeds as in acid solution with 2·5 atoms of oxygen available per molecule of $KMnO_4$, although such is not literally the truth.

To completely oxidise phenol, 14 atoms of oxygen are required, according to the following equation:— $C_6H_5OH + 14O = 6CO_2 + 3H_2O$. Since only 2·5 atoms of oxygen are available per molecule of $KMnO_4$ then 5·6 molecules of $KMnO_4$ would be required for every molecule of pbenol, and the factor for N/10 $KMnO_4$ in terms of phenol becomes:—

$$\frac{\text{Mol. wt. phenol}}{2{\cdot}5 \times 2 \times 10 \times 5{\cdot}6 \times 1000}.$$

Experiments with a phenol solution containing 0·0005 grm. of phenol per cc., as determined by the Koppeschaar bromine method, resulted as follows:—

Ex. No.	Grm. phenol taken.	Per cent phenol found.
1.	0·0050	99·65
2.	0·0050	100·18
3.	0·0075	99·65
4.	0·0076	99·86
5.	0·0100	99·86
6.	0·0100	99·72

Now, when the cresols were run in the same manner as phenol it was found that they were not completely oxidised and that they varied slightly as to the rate with which oxidation proceeded; hence, any permanganate method for their accurate determination must depend upon definitely fixed condltions.

Likewise, it was obvious that commercial creosote and guaiacol could not be determined by this procedure, since they are mixtures of several more or less related phenols that are not present in like proportion in different specimens. However, with single solutions of several common phenols and closely related compounds, fairly gratifying results were obtained. Pyrogallol, pyrocatechin, resorcinol, and hydroquinone, from all of which the CH_3 group is absent, were readily and completely oxidised.

Benzoic acid was very slightly attacked, while under similar conditions salicylic acid and salol were completely oxidised. Thus it would seem that the phenolic OH group predisposes towards a complete oxidation, and that many uninvestigated phenols and closely related compounds would give analogous reactions. In making up solutions of the several phenols, sufficient N/2 NaOH was added when necessary, to ensure ready solution. The following table is self explanatory:—

Substance.	Percentage found.	
Pyrogallol	100·4	100·1
Pyrocatechin	100·2	99 9
Resorcinol	100·5	100·4
Hydroquinone.. ..	99·49	99·56
Salicylic acid	99 79	100·2
Salol	99 77	99·91

The alkaline permanganate method is especially applicable for the quantitative estimation of the above compounds when they occur individually in very small amounts in single solutions, or in conjunction with substances not readily oxidised.

A REPRESENTATION OF THE CHEMICAL ELEMENTS BY MEANS OF POINTS IN ORDINARY SPACE.

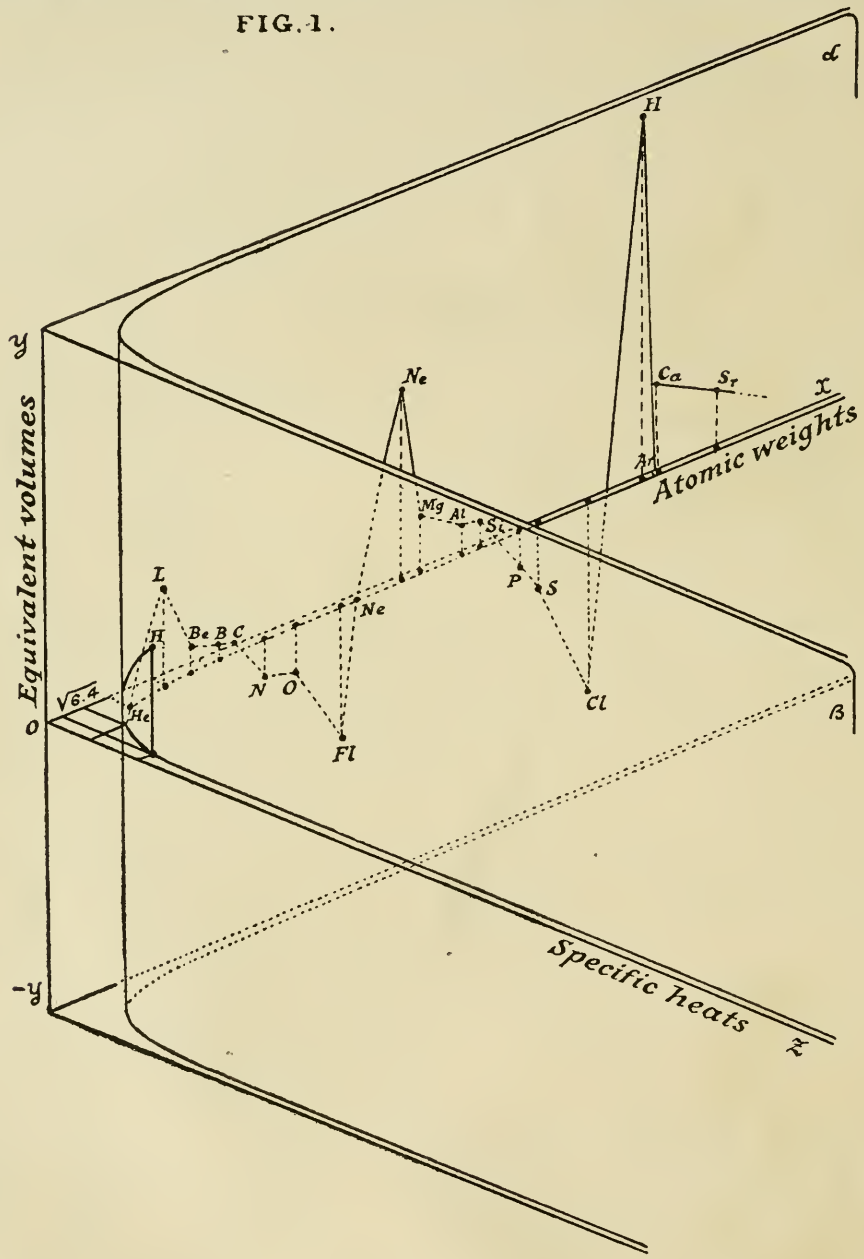
By ARNALDO PIUTTI.

THE representation of the chemical elements on the plane of two rectangular axes, x, y, by means of points on the said plane, being based on the numerical values of two properties only, or on the quotients of these values, does not admit of extensive generalisations.

Our knowledge would undoubtedly make a notable advance in this direction if methods of representation could be used in which all the known properties of the elements which are measurable and can be expressed by numbers could be taken into consideration, but this would necessitate representing them by points in spaces of more dimensions than ordinary space, either by geometrical figures drawn on planes (if a graphic representation were required) or by means of models (if a representation in space were required), in the way in which in descriptive geometry the shapes of bodies existing in three, four, or n dimensions are represented on a plane.

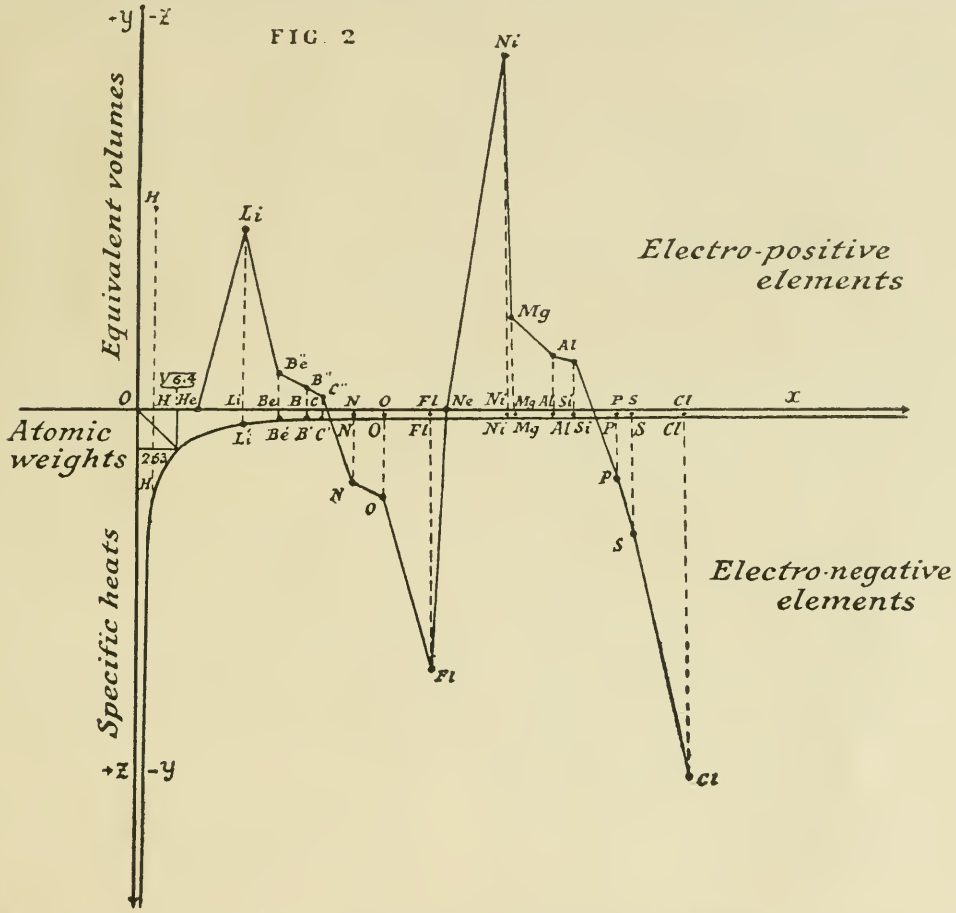
Thus such methods of representation are as yet im-

FIG. 1.



possible, both owing to the fact that we have not yet obtained many numerical data referring to the properties of the elements, and moreover because these sometimes exist in many forms, so that we do not always know how to choose their constants correctly. Therefore, taking the representation of them in a plane, originally due to Borchers ("Die Beziehung zwischen den äquivalenten Volumen und Atomgewicht," Halle-a.-S., Wilhelm Knapp), and afterwards modified by C. Schmidt ("Studien über das Periodische System," *Zeit. Phys. Chem.*, 1904, lxxv., 651) by considering the elements as having positive or negative ordinates, according as they are electropositive or electronegative (whence it follows that the neutral elements are situated on the axis of x), I have limited myself to constructing a spacial representation, using, in addition to the

FIG. 2



values employed by the above-mentioned authors, the values of the specific heats of all the elements measured on a third co-ordinate axis in the following way. In working out this scheme I have availed myself of the great skill of my colleague, Prof. Del Re, and have been aided by my assistants, Magli and Perrier, to whom I owe hearty thanks.

Taking a third orthogonal axis of co-ordinates (Fig. 1) arranged in the usual way, and denoting, as in the diagrams of Borchers and Schmidt, by x the axis on which are measured the atomic weights, and by y that on which the equivalent volumes are measured, on the third axis z I have marked the specific heats of the corresponding elements, taken if possible at temperatures lying between 0° and 100° (Landolt-Börnstein, "Physikalische-chemische Tabellen," Berlin, J. Springer, 1905; "Tables Annuelles de constantes et données numeriques," vol. i., 1910;" "Recueil de constantes physiques," H. Abraham et P. Sacerdote, Gauthier-Villars, Paris, 1913).

Then applying the law of Dulong and Petit, according to which the product of the atomic weight and specific heat can be regarded as nearly constant and equal to 6·4 (atomic heat), I have hence immediately deduced that on the plane $x z$ the elements represented are projected as points the co-ordinates of which satisfy the equation $x z = 6{\cdot}4$, which is an equilateral hyperbola with the x and z axes as asymptotes.

Hence it follows that the points representing the elements *are situated on the surface of a hyperbolic equilateral cylinder*, the right section of which is the above hyperbola; in place of it we should obtian another hyperbola if we substituted another value for the constant 6·4, owing to the variation of the specific heat in dependence on the temperature. And since atomic weights and specific heats are numerically essentially positive, the said points lie on one side only of the cylinder.

If now we consider the (straight) line which is the locus of the vertices of corresponding right sections we shall find points which are on one side of the line and points which are on the other side; and those on the one side are those for which the atomic weight is greater than $\sqrt{6{\cdot}4}$, *i.e.*, 2·53 (which amounts to saying that the specific heat is less than 2·53), and those on the other are those for which the atomic weight is less than $\sqrt{6{\cdot}4}$ (and hence the specific heat is greater than $\sqrt{6{\cdot}4}$).

The line would then be the locus of the points repre-

senting the elements which would have an atomic weight equal to their specific heat.

Hence arises the necessity for keeping distinct the two parts into which the line divides the surface of the cylinder of representation. For the present we will call the first semi-surface the α surface, and the second the β-surface.

Now the fact that only hydrogen is situated on the β-surface, while all the other elements yet known are arranged on the α-surface seems to me to be noteworthy; for hydrogen takes up its position thus in a spacial representation based on a property which it has in common with the other elements (atomic heat). This does not occur in the planar arrangements of Borchers and Schmidt, nor is it shown in the periodic system of Mendeleeff and L. Meyer, whilst an element which is so important and so widely distributed would be expected to take up its position among the other elements, whatever method of arrangement was chosen.

The suggestion of Mendeleeff that it should be placed at the head of the alkali metals was not confirmed by its properties in the solid state, afterwards observed by Sir J. Dewar; nor can the proposal made by him, to put it among the metalloids (*Comptes Rendus*, 1899, cxx., 451), for example at the head of the halogens, be accepted, since its properties are so different from theirs.

For this reason J. W. Retgers (*Zeit. Phys. Chem.*, 1895, xvi., 646) and L. Meyer (*Liebig's Ann.*, 1870, Suppl. vii., 357) have suggested excluding it from the periodic classification, and giving it an exceptional position, and E. J. Mills ("Numeric of the Elements," *Phil. Mag.*, 1884, [5], xviii., 393; 1886, xxi., 151) and Rudorf (*cf.*, "Das Periodische System," Leopold Voss, Hamburg and Leipzig, (1904), p. 83) have explained the fact by considering it as the last representative of a group of gases of the type of Argonian, Alnitamian, and Crucian, &c. (*Idem.*, p. 281), discovered by Sir Norman Lockyer in the fixed stars (gases of the stars λ 4451, 4457, 4649·2 respectively), and no longer existing in the solar system, or of another group called protometals (Asterium) by English astrophysicists.

And since it would be singular that one element only, viz., hydrogen, should take up its position on one semi-surface of the hyperbolic cylinder while all the others accumulated on the other, or, in other words, that elements with atomic weight less than $\sqrt{6{\cdot}4}$ would not have had, or would not still have, any other representatives, on the same semi-surface β would be found the points representing the proto elements which belong to our solar system, and from which, according to the recent theory of J. W. Nicholson (*Phil. Mag.*, 1911, xxii., 864—889), all the others are derived; for example, coronium (at. wt. 0·5131) and protofluorium (at. wt. 2·3604), to which are due some lines in the spectrum of the solar corona, and nebulium (at. wt. 1·6273) which is seen in the spectrum of the nebulæ and which, according to Nicholson's calculations, has an atomic weight lower than $\sqrt{6{\cdot}4}$, *i.e.*, 2·53, and hence must have a high specific heat like that of hydrogen.

According to this theory of Nicholson's these elements, with hydrogen, the only long-lived one on our planet, would constitute the primordial form of matter, from which all the other elements are derived, by attributing to them atomic weights deduced on a simple electron theory by equally simple combinations, particularly in the case of elements of low atomic weight. The agreement thus obtained with the experimental values is so good that we are forced to admit that it cannot be due to chance.

The grouping of the elements on the semi-surface of an equilateral hyperbolic cylinder deduced from the law of Dulong and Petit would to a certain extent confirm the views of Nicholson, besides being in harmony with the periodic system and with the arrangement given in it of the other elements, without excluding any, since those which come from radioactive transformations, according to F. Soddy (CHEMICAL NEWS, cvii., 97), A. S. Russell (*Idem.*, p. 49), and K. Fajans (*Le Radium*, x., 61) find their places in this classification.

Finally, to give in addition to the perspective representation which results from Fig. I. another which renders possible the direct measurement on the plane of the diagram of the constants relating to the different elements (and hence the immediate to return to the spacial determination) we may institute in the plane a system of co-ordinates of x, y, and x, z; in this system the directions of Prof. Del Re (*cf.*, "Sulle forme fondamentali dello spazio rigato, sulla dottrina degli immaginarii e sui metodi della geometria descrittiva"; L. Albano, *Accad. della Scienze*, Napoli) are followed; that is to say, a line is drawn in the plane of the diagram and an origin O is marked on it and a positive direction O X, and the perpendicular to O X is drawn through O. O X and O Y, one of the lines drawn from O, are taken as the positive direction of the system x, y, and O X and the other line through O, O Z, as the positive direction of the system x, z.

In the case of any element M, as was said before, on the axis O X, starting from O, its atomic weight x is marked, and on the axis O Y (in the positive or negative direction, according as the element is electropositive or electronegative) its equivalent volume y, and on the axis O Z its specific heat z, and thus two points are obtained, M′ and M″, the co-ordinates of which are x, y, and x, z respectively. These give the couple M′M″ which, as in Monge's system, represent the element M in space.

(*Note.*—In Fig. 2 the elements are marked in ascending atomic weights, ending with chlorine, for the present neglecting the position of hydrogen with regard to the other elements).

Doing this for all the elements as many points are obtained as elements are taken into consideration. They represent an arrangement the projection of which on the plane $x\,y$ is the configuration of Schmidt, while its projection on the plane $x\,z$ is the equilateral hyperbola, having for asymptotes the axis of x and the axis of z, and for semiaxis $2{\cdot}53 \times \sqrt{2}$.

As I have previously shown, our actual knowledge of the constants of the elements leads us to the conclusion that in the hyperbolic cylinder of representation only one side is utilisable; but if in cosmic conditions differing from the present elements would be able to exist with negative physical constants their representative points would evidently be found on the other surface.

I have wished to present to the Academy a preliminary notice of my attempt to represent in space the chemical elements, reserving to myself the right to develop it later as the revision of their constants or new determinations furnish me with the necessary data.—*Rendiconti della R. Accademia dei Lincei*, xxii., Series 5a, [i.], No. 9.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

(Concluded from p. 71.)

V. *Effect of Organic Addition-agents in Tin Electrolytes.*

THERE should be little difficulty in obtaining thin smooth adherent deposits of tin; but when the deposition is carried to an appreciable thickness, difficulties arise. The electrodeposits of tin have a tendency to become crystalline and brittle, more and more so the longer the electrolysis is continued (Barclay and Hainsworth, "Electroplating." 1912 Ed., p. 233).

The physical condition of electrolytically deposited metals is economically of the most importance, since the metallurgist, as well as the electroplater, wants a coherent dense smooth deposit, as the purity of the cathode metal

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii.. No. 6.

depends upon its density and smoothness; and, besides, the ampère-hour efficiency of a refinery is dependent upon the prevention of short circuits between anodes and cathodes. As a rule, the rougher the cathodes the lower the ampère hour efficiency and the less pure the refined metal.

The characteristic form of tin, deposited from acid electrolytes, is a mass of loose non-adherent crystals. This tendency is less apparent in neutral and in alkaline electrolytes. The concentration of the electrolyte, the temperature of the electrolyte, and the current-density, each have an effect on the character of the deposit. In general, the more concentrated the electrolyte up to saturation, and the higher its temperatures, the more coherent and smoother the deposit. Another factor influencing the deposition is one which is the result of the presence of certain organic addition-agents, which change the character of the deposit either beneficially or detrimentally.

The effect of addition-agents, when properly selected, is to cause the deposit to be smoother, denser, and more adherent. When not properly selected, the opposite effect will result—that is, the deposit will be more crystalline and less adherent, or collect as a spongy mass which drops from the cathode.

It has been found that the addition of glue or gelatin to certain tin baths, in the proportion of 1 part by weight to 1000 parts of electrolyte, has a remarkable effect on the character of the deposited tin, and, at the same time, allows the use of a higher current-density. Other addition-agents which have been found to be beneficial for certain electrolytes are glucose, saccharine, acetone, and organic salts of aluminium and iron. The effect of organic addition-agents is not permanent, so in all cases, when used, further additions must be made periodically (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electrodeposition," 1911 Ed., p. 215).

1. Hollis's U.S. Patent 916,155 is for the use of an electrolyte containing tin fluosilicate, and to which gelatin or glue is added for the purpose of increasing the density of the deposit (*Electrochem. and Metallurgical Ind.*, 1909, vii., 224).

2. German Patent 244,567, to Matuschek, is for an electrolyte consisting of a concentrated solution of ammonium oxalate saturated with tin-ammonium chloride ($SnCl_2.2NH_4Cl$), to which an addition of black-oak tannin (quercitrinic acid) has been added. The electrolyte which he used was prepared by dissolving 200 grms. of stannous-ammonium chloride in 600 cc. of a concentrated solution of ammonium oxalate, then the addition of 50 grms. of black-oak bark tannin. This solution was electrolysed at ordinary temperature, and a solid deposit of tin was produced, when current-density of 28 ampères per sq. ft. (3 amp. per sq. dm.) was employed. The statement is made that other additions may be made to the bath, such as sodium dihydrogen phosphate, sodium silicofluoride, an inorganic acid other than nitric acid, preferably hydrofluosilicic acid, or a mixture of borax and hydrofluosilicic acid. As an example of a bath of this composition, there was added, instead of 50 grms. of tannin, to the bath given above, 6 grms. of tannin and 6 grms. of sodium dihydrogen phosphate. This bath was found to be more constant than the first.

Claims were made that much higher current-density can be employed and the electrolysis be conducted at ordinary temperature, and the deposited tin still form solid and adherent, which is not possible by using the generally employed hot alkaline electrolytes. An E.M.F. of 2 to 3 volts was maintained between electrodes 13 cm. (5⅛ ins.) apart, and good deposits continued to form.

The electrolyte is said to be suitable for the refining of tin, electroplating of tin, and electro-detinning of tin-plate scrap. The addition of ammonium salts, such as ammonium chloride, and organic substances, such as carbohydrates or gums, &c., is desirable for the production of brilliant deposits (*Metallurgie*, 1912, ix., 492; *Journ. Soc. Chem. Ind.*, 1912, xxxi., 440).

3. Steiner found that tin deposited from sodium sulphostannate electrolytes (see Sect. IV., 11) "could be still improved by adding a colloid to the electrolyte, for example, gelatin, as is used in the Betts process for electrolytically refining lead."

4. E. F. Kern and A. P. Frapwell conducted experiments on the effect of certain organic addition-agents on the character of electrolytically deposited tin from solutions of sodium-stannous chloride, stannous fluoride, and sodium-stannous fluoride. (Results have been previously published). These salts were selected on account of their solubility, and because their solutions are highly ionised and are excellent conductors.

(*a*) *In Sodium-stannous Chloride Electrolyte.*—The solution was prepared to contain about 80 grms. of tin and 50 grms. of sodium, as chlorides, per litre, by dissolving a calculated amount of sodium chloride in water, then adding a calculated amount of stannous chloride crystals. The electrolysis was conducted at ordinary temperature, using cast-tin anodes and tinfoil cathodes, with current-density of 10 ampères per sq. ft. (0·9 amp. per sq. dm.). The distance between electrodes was about 1½ in. (3 cm.), and potential about 0·1 volt. The deposit formed as a mass of bright needle crystals, which soon short-circuited the electrodes.

The effect of three addition-agents — gelatin, gum-arabic, and tannin—was investigated, the electrolysis being conducted at the same temperature and current-density as above.

The presence of gum-arabic, in the proportion of 1 grm. per 800 to 1200 cc. of solution, caused the deposit to form as small bright adherent crystals, which did not short-circuit the electrodes. The electrolysis was conducted for periods of one to three hours. The gum-arabic was added as an aqueous solution. It did not cause a precipitate to form when it was added to the electrolyte.

The addition of a solution of gelatin, and of tannin, caused a white colloidal precipitate to form when added to the electrolyte. The deposit formed from electrolytes, to which the gelatin and the tannin were added in the proportion of 1 grm. per 500 to 1500 cc. of electrolyte, were a mass of small bright needle crystals which could be rubbed off with a stirring rod. These two addition agents caused the tin to be deposited as very small needles, whereas the deposits formed in the solutions which contained no addition were long dendritic needles.

(*b*) *In Stannous Fluoride Electrolyte.*—The solution was prepared by dissolving a weighed amount of stannous chloride in a small volume of water and adding a few cc. of hydrochloric acid to clear the turbidity. The tin was then precipitated by the addition of a concentrated solution of sodium carbonate, which gave a precipitate of stannous hydroxide. This was washed free of alkali by decantation, and finally filtered. It was dissolved in moist condition in a measured quantity of 40 per cent hydrofluoric acid, to give a solution containing a very slight excess of acid. This concentrated solution was diluted, so as to contain about 80 grms. of tin per litre.

The electrolysis was conducted at ordinary temperature, using wax beakers for the cells, and cast-tin anodes and tinfoil cathodes. The current was passed at 10 ampères per sq. ft., with the electrodes about 1½ in. (3·8 cm.) apart, and E.M.F. of 0·15 to 0·16 volt. The electrolysis was carried on for periods up to eight and a-half hours.

The deposits formed, with no addition-agent present, as a mass of loosely adherent sparkling dendritic needles, which soon caused short-circuiting. The anodes were evenly corroded, and remained very bright throughout the electrolysis.

The addition-agents tried were solutions of tannin, gelatin, gum-arabic, glycerin, resorcin, saccharine, grape-sugar, and glucose. The deposits were not much altered by any of the addition-agents except tannin, gum-arabic, resorcin, and glucose. Tannin proved to be the most

effective, and resorcin and glucose less effective than either the tannin or gum-arabic. The additions were made in small amounts of the aqueous solutions at a time, the first addition being in the proportion of 1 grm. per 2000 cc. of electrolyte, then 1 grm. per 1500 cc. of electrolyte, and so on by a 500 cc. decrease in the proportion of the electrolyte, until finally 1 grm. of the addition-agent per 100 cc. of the electrolyte had been added.

In the case when tannin was used, 1 grm. per 1500 cc. of electrolyte caused the deposit to form finely crystalline and adherent. The best deposits formed when tannin was present.

The presence of gum-arabic in the proportion of 1 grm. per 1500 cc. electrolyte caused a marked improvement in the deposition. Large proportions did not prove beneficial. In no case was a dense smooth deposit formed.

With resorcin and glucose, not much improvement resulted until they had been added in the proportion of 1 grm. per 100 cc. of electrolyte, and even then the crystalline deposition was not restrained.

(*c*) *In Sodium-stannous Fluoride Electrolyte.* — This electrolyte was prepared in the same manner as the stannous fluoride electrolyte, with the addition of sodium fluoride. The solution contained 80 grms. of tin and 50 grms. sodium in the form of fluorides.

The electrolysis was conducted at room temperature (20° to 23° C.) in the same manner as the stannous fluoride electrolyte, but in this instance operating at current-density of 15 ampères per sq. ft. (1·4 amp. per sq. dm.). The electrodes were placed 1¼ in. (3 cm.) apart, and the E M.F. averaged 0·18 volt. The deposit formed as bright dendritic needles, which soon short-circuited the electrodes.

The same addition-agents were used as for the stannous fluoride electrolytes, they being added at regular intervals in small amounts at a time, until an apparent change in the characteristic appearance was noticed.

Tannin in the proportion of 1 grm. per 2000 cc. of electrolyte caused the deposition of a smooth very crystalline firmly adherent coating. The run was continued for periods of six and a-half hours. The anodes corroded evenly and remained bright. The potential between electrodes varied from 0·24 to 0·26 volt. Current-density of 15 ampères per sq. ft. (1·4 amp. per sq. dm.).

Gelatin in the proportion of 1 grm. per 1000 cc. electrolyte caused the deposit to form as adherent small crystals, with a few small dendrites on the edges of the cathode. It is not so satisfactory an addition-agent as tannin.

DETERMINATION OF HYDROGEN, NITROGEN, AND METHANE IN GAS BY COMBUSTION IN A QUARTZ TUBE.*

By Prof. MATHERS and IRA E. LEE.

THE purpose of this research was to devise a more convenient and a more accurate method for the determination of hydrogen, nitrogen, and methane in gas. Many different methods have been advocated for making this analysis ("Review of Progress in Gas Analysis," *Chem. Zeit.*, 1908, xxxii., pp. 801, 817). The combustion of these gases by explosion with oxygen in an explosion pipette was the method generally used until a few years ago. Results with this method in this laboratory have been very unsatisfactory. The difficulty has been that the gases were not completely burned. This gives a result for nitrogen which is too high and causes the gas to appear worse than it is.

A much better method employs the Winkler-Dennis pipette, in which the gas residue is treated with an excess of oxygen in the presence of a platinum spiral which is heated to redness by a current of electricity. This method, we think, gives accurate results when all of the conditions are favourable. The great difficulty is in fastening the spiral in such a way that no metal except platinum is exposed to the action of the hot oxygen. Base metals such as iron are readily oxidised by the oxygen. This introduces a serious error into the work. If the platinum wire for electrically connecting the coil is sealed through glass at a point near the heating coil, the glass at the joint is almost certain to crack. In most forms of the apparatus, the platinum spiral is fastened to stout iron wires which are inclosed in glass tubes. These tubes enter the pipette through holes in a rubber stopper. A cement is used to make the iron wires in the glass tubes gas tight. This form of apparatus would be satisfactory if platinum wires were used in the place of the iron wires, but this is too expensive. The ends of the iron wires in the pipette are oxidised during each combustion. This error increases the percentage of hydrogen and lowers the percentage of nitrogen. A modification of the apparatus, as devised in this laboratory, overcomes these objections and difficulties. Two short pieces of platinum wire were sealed into the ends of two glass tubes. The platinum spiral which was to be heated was fastened to two platinum wires, which were then thrust in the open ends of the glass tubes. These wires extending into the glass tubes were bent into wavy shapes, so that they would be held in position by contact with the sides of the tubes. When the pipette was filled with mercury, these glass tubes were filled (and remained filled) with the mercury, so that the electrical connection was complete from the outside platinum terminals through the platinum spiral. The places where the platinum wires were sealed in the glass were so far from the heated spiral that there was no trouble with cracking. A platinum spiral, made by twisting together several very small platinum wires, lasts much longer than a spiral made of a single platinum wire. The spiral must be smaller in diameter than any of the other pieces of platinum which are used. This apparatus gives correct results when properly manipulated.

One source of error is always present in all combustion over mercury. If the spiral is heated too hot, the mercury is oxidised, while if the temperature is so low that there is no danger of oxidising the mercury, the combustion of the gases will be incomplete. The Drehschmidt method (Hempel-Dennis, "Gas Analysis," p. 140) avoids this error, since no mercury is present during the combustion. This method of burning the gas residue mixed with oxygen, by passing it through a hot platinum capillary tube, is perhaps the best scheme. However, the high cost of the platinum capillary tube, together with the rapid deterioration of the apparatus, makes a modification desirable. The experiments described in this paper show that the quartz tube filled with pieces of scrap platinum is an entirely satisfactory substitute for the platinum capillary tube in the Drehschmidt apparatus.

The quartz tube was 30·5 cm. long, 7·25 mm. outside, and 3·38 mm. inside diameter. Its volume, determined by the weight of mercury required to fill it, was 3·317 cc. The platinum scrap, which was used as a contact substance in the quartz tube, was prepared by cutting pieces of ordinary scrap platinum wire, which every laboratory has in quantity, into as short pieces as possible with shears. These small fragments were then placed upon stiff paper which passed through a cornet roll mill a number of times. These flattened pieces of platinum presented a large surface to the passing gas, and at the same time offered very little resistance to the passage of the gas. Two pieces of scrap platinum gauze were used, one in each end of the quartz tube, to keep the small pieces of platinum in position. The platinum weighed 11,189 grms., and had a volume of 0·522 cc. The platinum occupied 21·6 cm. of the length of the tube.

The data concerning the many preliminary experiments, which merely served to detect the errors, will be omitted.

* Paper presented at the Fifth Annual Meeting of the Indiana Gas Association, Indianapolis, Ind., March, 1913. From *Chemical Engineer*, xvii., No. 4.

The following form of apparatus and manipulation were found satisfactory :—

A mercury pipette, holding the gas to be burned and the oxygen required for the combustion, was connected to one end of the quartz tube by a suitable capillary tube with rubber connections. A mercury burette, arranged to receive the gas, was connected to the other end of the quartz tube in a similar manner. Pinch-cocks, one on the burette and one on the pipette, controlled the connections with the quartz tube. The burette was provided with a water-jacket, which was connected at its lower end with a level bottle, so arranged that the water could be drawn out and then passed back into the water-jacket. This circulation and thorough mixing of the water were necessary to prevent unequal temperatures between the top and bottom of the burette. The water-jacket was improvised from the outside part of a Liebig condenser. A thermometer, which showed the temperature of the water and gas, was suspended about midway of the burette inside of the water-jacket. The quartz tube was heated by a Bunsen burner provided with a wing tip which produced a broad flame. An asbestos board was suspended about 5 mm. above the quartz tube, to lessen the radiation of heat. The manipulation was: The temperature of the gas in the pipette—that is, the temperature at which it was measured—was carefully read. The pinch-cock connecting the burette to the quartz tube was opened and the burner was lighted for three minutes. The increase in volume of the air in the quartz tube produced by the heat was cared for in the burette. The pinch-cock connecting the pipette to the quartz tube was opened and the level bottle was raised so that the gas and oxygen passed slowly and regularly over the glowing platinum, generally about three minutes being required. In no case was there any indication of an explosion in the pipette, even when the velocity of the gas was greatly increased. The level tube on the burette was raised and the level bottle on the pipette was lowered so that the gas was forced back from the burette into the pipette. The gas was then again passed through the quartz tube over the glowing platinum into the burette. The flame and the asbestos board were removed and water was poured upon the quartz tube to cool it. After the quartz tube had reached room temperature, the pinch-cock connecting the burette and quartz was closed. The mercury in the burette and level tube was levelled. The water in the water-jacket was passed back and forth by means of the level bottle until the thermometer in the water-jacket showed constant temperature. The mercury in the burette and level tube was again carefully levelled and the volume of gas was read. The final gas volume was always corrected for variation from the initial temperature.

The process as described above was tried with pure hydrogen gas, which was prepared by the action of boiled dilute sulphuric acid upon pieces of zinc contained in a gas double pipette for solids. The pipette was filled with boiled distilled water to displace the air. The sulphuric acid was added through a glass tube which entered through the opening for the introduction of solids into the pipette. The hydrogen gas was allowed to escape completely from the apparatus several times before any was saved for analysis. This form of generator very effectively protected the hydrogen gas from the diffusion of air. The results are given in the following table :—

Hydrogen used	26·02	21·06	20·4
Air added	90·6	77·9	77·9
Volume after combustion ..	77·6	66·75	67·7
Time of experiment, minutes	2·5	2·3	3·5
Total experimental	39·03	31·6	30·6
Contraction theory	39·03	31·59	30·6

The following table shows the results which were obtained in the analysis of gas residues :—

Residue (cc.)	51·9	52·3	58·73
Oxygen (cc.)	80·4	71·3	67·18
Volume after combustion ..	50·2	42·4	38·0
Time	—	3	2
Total contraction	82·1	81·4	81·34
Carbon dioxide	18·8	17·5	17·77
Hydrogen	28·4	29·4	29·0
Nitrogen..	4·7	4·25	3·9

The result in experiment 1 was obtained with the ordinary combustion pipette. This value was taken as a standard. Experiment 2 in the table shows 17·5 per cent of carbon dioxide, which was, of course, obtained by the absorption of the carbon dioxide which was in the burette. This value must be corrected for the amount of carbon dioxide which remained in the quartz tube. The total gas residue after combustion (including the air originally in the quartz tube) was 42·4 plus 2·795 (the volume of the quartz tube which was unoccupied by platinum), which was 45·195. So, 93·8 (42·4—45·195) was the per cent of the gas which was measured in the burette. The carbon dioxide in all the gas after the combustion was 17·5—93·8, or 18·65 per cent. All carbon dioxide readings were corrected in this manner. The variations of the results in experiments 2 and 3 from the standard in experiment 1 are small and perhaps due to changes in the gas, since the three experiments were made on three successive dates. To avoid this variation from day to day, several gas residues were prepared for analysis one after noon, were mixed in a water pipette, and portions of this mixture were used for analysis. The results are :—

Residue	49·92	49·95	49·90
Oxygen	68·8	68·9	68·9
Volume after combustion	41·5	41·55	41·6
Time	2·0	3·5	3·5
Total contraction	77·22	77·3	77·2
Carbon dioxide	18·65	17·45	17·6
Hydrogen	26·6	26·65	26·5
Nitrogen	4·69	4·64	4·7
Methane	18·65	18·66	18·70

All of the results given in the tables show that the quartz tube is as accurate as the combustion pipette. It was found necessary to pass air through the quartz tube to remove the carbon dioxide produced by one experiment if another experiment were to be made at once. If only total contraction was desired, the carbon dioxide did not need to be removed. If nitrogen was to be determined, the gas remaining in the tube from previous experiment had to be removed by passing air.

This apparatus gave an excellent method of determining the total nitrogen in gas. The gas was mixed with an excess of oxygen whose nitrogen content was accurately determined. After combustion in the quartz tube, the gas was passed into potassium hydroxide to take up the carbon dioxide, and alkaline pyrogallol to take up the excess of oxygen. The unabsorbed residues consisted of the nitrogen in the gas and the nitrogen which was in the oxygen. The results are as follows :—

Gas	49·9	50·0	49·93
Oxygen	76·4	74·05	78·04
Nitrogen added in oxygen ..	7·10	6·95	7·19
Total nitrogen	8·68	8·62	8·78
Nitrogen in gas taken	1·58	1·67	1·59
Nitrogen per cent in gas ..	3·17	3·34	3·20

Other tests showed that under the conditions of the experiment less than 67·7 of the oxygen (63·4 cc. of pure oxygen) did not give complete combustion with 50 cc. of the gas. This was 12 cc. of pure oxygen in excess.

Since the work which is described in this paper was completed, Hempel, a German authority on gas analysis, has published the same method, except that he heated the quartz tube with a blast lamp. He also described an arrangement for heating a platinum spiral inside a quartz

tube with electricity. Electrical connections were made by sealing platinum wires into glass capillary tubes, which were then attached to the quartz tube by rubber tubing. Hempel says that the older methods of burning the gas were never accurate because the temperature of the platinum spiral was never high enough. He thinks that these methods which use the quartz tubes (or the platinum capillary) are the only ones which give accurate results.

After considering all of these results, one feels that the older methods of determining hydrogen, nitrogen, and methane are about to be supplanted by a new and more accurate method.

Summary.—Gas residues, after the addition of oxygen gas, were burned by passing them through a heated quartz tube which contained pieces of scrap platinum. The results are very accurate. The advantages of this apparatus over the standard combustion pipettes are :—

1. The quartz tube and pieces of platinum are not easily broken or damaged during use. The quartz tube is brittle, but will break only if struck a blow. The combustion pipette is very easily broken, and the small platinum wire often burns out, even when great care is exercised by the operator.

2. No metal or other substance which can be oxidised or acted upon by any of the gases is present in the quartz tube during the burning. In the combustion pipette, mercury, an oxidisable metal, is always present. In some of the experiments during the research, the conditions were such that very serious errors were made by the absorption of gases by the mercury. Everyone is familiar with the formation of oxides upon the mercury and upon the sides of the combustion pipette.

3. Small cracks in glass tubes, or leaks around the rubber stopper or places where glass tubes enter in the combustion pipettes, cause serious errors. There is very little chance for leaks in the quartz tube apparatus.

4. Platinum scrap, such as short lengths of wire, which we generally find plentiful in laboratories, is used in this apparatus. The quartz tubes are cheap.

5. The temperature in the quartz tube may be made high enough to insure complete combustion of the gases.

The disadvantages of this new process are :—

1. The gas becomes heated during the combustion, so care must be taken to determine the final temperature at which the gas is measured. Corrections must be made for all temperature changes.

2. A correction must be made for the carbon dioxide which remains in the quartz tube after the combustion. This disadvantage can be overcome, perhaps, by the use of a smaller bore capillary quartz tube, in which the volume is so small that a correction is unnecessary.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

The Speed of Hertzian Waves.

The researches made by physicists of all countries have proved that the Hertzian waves are propagated with the same speed as light, that is to say, at about 300,000 kilometres a second. Three French scholars, M. Abraham, Professor at the Conservatoire des Arts et Métiers, Major Ferrié, and M. Dufour, have, under the auspices of the Bureau of Longitudes, just determined the speed of propagation of the Hertzian waves between Paris and Toulon. Part of the results has been calculated and the speed found is 295,900 kilometres to the second, with a difference of less than 1 per cent for each determination, in comparison to the average. When all the experiments are terminated, it will be possible to have a precision of ½ per cent.

MM. Abraham, Dufour, and Ferrie propose to continue their experiments, and to study the speed of the propagation of Hertzian waves between two points separated by the sea. They intend to measure this speed between the Eiffel Tower and the Station of Wireless Telegraphy at Washington, whilst the longitude of the capital of the United States is being determined.

Intense Cold can be Easily Obtained.

The well-known engineer, M. George Claude, has just indicated a means of obtaining the very low temperatures (so much sought after at present) by the help of liquid nitrogen that can be very easily procured in the manufactories that produce liquid air. The fact is, that by bubbling a current of hydrogen in liquid nitrogen, it is easy to obtain in vessels open to the free air the temperature of −211°, which corresponds to the solidification of the nitrogen, and thus presents the advantage of constituting a veritable fixed point.

Forest Fires.

With the first great summer heats the forest fires become so frequent that the National Society of Agriculture of Paris has considered it both prudent and urgent to seek after serious means of circumscribing them by national defences and by almost totally annihilating their effects.

M. Marchal had recently proposed to the Society conter-igniferous or fire-resisting plantations, separating the forest trees by blocks or islets. M. Rivet, Professor at the Agronomic Institute, has just taken up again this excellent project and given it his support. With M. Marchal, he proposes plantations of ivy, cactus, and other fire-resisting plants of which should be formed isolating hedges.

M. Audiffred, President of the Society of Agrieulture, has asked for the reports of these two specialists to be published. These reports will undergo a special study, the results of which will shortly be submitted to the consideration of the Minister of Agriculture, so as to enable the rapid establishment of a general plan for the protection of our forests against fire.

The Vegetable Riches of Morocco.

M. Pitard, Professor at the Natural History Museum of Paris, has just made a most interesting journey to Morocco. The botanical exploration of the Chaonia region has enabled him to discover the presence of 850 vegetable species, of which 657 are dicotyledons, 180 monocotyledons, 2 coniferæ, and 11 pteridophytes. This flora offers a very striking analogy with that of the Algerian Tell, and though less striking still distinctly accords with the flora of the Spanish Peninsula, which is a proof that relations relatively recent and easy existed between these two regions. At any rate, the want of numerous points in common between the flora of Chaonia and that of the Canary Isles is not a sufficiently decisive argument in favour of the non-existence of the Atlantide, for the fact is that the real canary flora being generally composed of mountainous plants, their absence in the Plains of Chaonia is natural enough, and if they exist anywhere it is on the heights of the Atlas.

Ultra-violet Action.

M. Victor Henri, Assistant in Professor Dastre's Physiological Laboratory at the Sorbonne, and M. René Wurmser have just developed a new theory concerning the action of co-ferments and of anti-ferments ; by the action of ultra-violet rays on oxygenated water and on sugars, it is found that poisons paralyse the action of ultra-violet rays in the same way as they paralyse the action of ferments. The action of poisons bears, then, on the substance to be transformed, and not on the ferment as has hitherto been believed.

Radium Fixes on to the Skeleton.

M. Dominici and M. and Mdme. Laborde have injected into animals radium salts in a soluble state, and have searched the place of fixation. Fragments of bone tissue having appeared constantly radioactive during the experiments, the experimenters have tried to make a precise departure between the quantities of radium fixed by the skeleton, the muscles, the viscera, and the skin.

A rabbit was killed thirty-three days after an intravenous injection of 0·06 mgrm. of pure radium associated with an

equal quantity of bromide of radium. All the skeleton separated from the muscles, tendons, then the muscles, viscera, and skin, have all been burned separately. The ashes, weighed and analysed, showed that the radium was fixed on the skeleton rather than on the other parts of the organism, where it is found in only very feeble quantities. In their communication to the Biological Society, MM. Dominici and Laborde conclude that it is very probable that the ingestion of radium salts would have the same effect.

Considering the well-known affinity of the skeleton for salts of calcium and strontium introduced into the organism, it is quite probable that salts of radium would also go, as in the above mentioned experiments, and be fixed on the skeleton.

The Salts of Uranium Hasten certain Reactions.

In their Laboratory of Chemistry at St. Cloud, MM. Daniel Berthelot and Henri Gaudechon have just remarked that the low average produce of certain photochemical reactions, which alone has prevented their practical application outside photography, may be corrected by the employment of very small traces of uranium salts acting as catalysers.

The Conductibility of Melted Salts.

M. Tissot has recently remarked that a great number of metallic salts previously melted, then solidified and cooled, become conductors under the application of a continuous potential difference of a few volts. The phenomenon presents the following characters :—At the moment of the application of a sufficient continued potential difference the system acquires a feeble conductibility, which increases, slowly at first, then more and more rapidly. When the thickness of the lozenge of melted salt is of the order of the millimetre, the frank conductibility is established only at the end of a few minutes, fifteen to twenty, for example ; but in thinner systems, that can be prepared by crushing a drop of melted salt between two platinum plates previously heated, the conductibility is more rapidly established and for a weaker potential difference. In all cases, and whatever may be the continuous potential difference applied to the system when it has become conductive, if electrical oscillations of sufficient intensity are made to act upon it, the conductibility immediately disappears. This discoheration is produced for an intensity of oscillations so much the weaker as the difference of the potential applied to the system is itself weak at the moment of the action of the oscillations. The system is, besides, apt to undergo a new coheration by the application of a suitable continuous potential difference. By leaving this difference applied during the action of the oscillation, the system can spontaneously coherate immediately the action ceases.

Although the coherers constructed up till now on this new principle are inferior as to sensibility and rapidity to those actually in use, the phenomenon is of a nature to interest physicists, for it presents a great generality. It has, indeed, been reproduced with the following salts :—Chloride of lead, chloride of thallium, bromide of cadmium, haloid salts of silver, and nitrate of silver.

Detection of Benzoic Acid in Presence of Phenols and Salicylic Acid.—Lucien Robin.—A very sensitive reaction for benzoic acid is the formation of a red amino compound when the acid is first nitrated, and the metadinitrobenzoic acid thus obtained is reduced by ammonium sulphide. A similar reaction is given by phenol, salicylic acid, &c., and hence these must be destroyed by means of potassium permanganate in sulphuric solution. The benzoic acid must be extracted by means of alcohol and sodium bicarbonate solution, the liquid must be evaporated, acidified with sulphuric acid, and heated to 80°, potassium permanganate being added drop by drop till the pink colour persists. The liquid is then allowed to cool, treated with ether, and again shaken with sodium bicarbonate solution. The benzoic acid is then detected as described above.—*Annales des Falsifications*, No. 55, 1913, p. 277.

NOTICES OF BOOKS.

A Manual of Painters' Colours, Oils, and Varnishes. By George H. Hurst, F.C.S. Fifth Edition. Revised by Noel Heaton, B.Sc., F.C.S., with a Chapter on Varnishes by M. B. Blackler, Ph.D. London: Charles Griffin and Co., Ltd. 1913.

This book has a well-deserved reputation as a text-book for the use of technical students and practical men, and the difficult task of revising another author's work has been so excellently carried out by the editor that it will undoubtedly for a long time retain its position among books upon the chemistry of paints. Every detail has undergone a careful revision, and while the original general plan has not been altered, in some cases it has been found necessary practically to re-write whole chapters. For example, the accounts of lead and zinc whites have been very greatly enlarged, and the general nature and properties of pigments are now treated more fully than before, while the chapter on varnishes has been extensively altered.

Natural Rock Asphalts and Bitumens. By Arthur Danby. London: Constable and Co., Ltd. 1913.

The author of this work has practically broken fresh ground in English literature, for no book has been published during the last twenty years upon rock asphalts, and his unbiassed account of the nature and uses of asphalts and bitumens has no rival in the language. The geology and history of the subject are treated very fully, the chapters on the latter being possibly rather overloaded with material, which, though interesting, is not of very great importance to practical or scientific men. After long accounts of the sources of asphalt in Europe and America, the extraction and preparation of rock asphalt is not reached until Chapter IX., more than half-way through the book. Here are given detailed descriptions of the practice in the mines, quarries, and factories of Eschershausen, Brunswick, followed by full and lucid accounts of modern work on methods of analysis. The author has had extensive experience of the employment of asphalt for various purposes, and states very clearly and definitely the conclusions he has come to and his reasons for them, when they differ, as they not infrequently do, from those of other authorities.

Die Anwendung Hoher Drucke bei Chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle. ("The Employment of High Pressures in Chemical Processes, and a Reproduction of the Method of Formation of Coal"). By Dr. Friedrich Bergius. Halle (Saale): Wilhelm Knapp. 1913. (M. 2.80).

In this monograph an account is given of the author's investigation of the effect of pressure upon chemical reactions, and the application of the results obtained to the case of the formation of coal. In many respects his work must be regarded as unfinished, and further experiments are necessary to throw light upon some points. On the other hand, from the study of the chemical and physical properties of superheated water certain definite conclusions as to the origin of coal may be drawn, and the author was well advised to publish the material he had accumulated, even although the research is by no means completed.

Physikalische Chemie der Homogenen und Heterogenen Gasreaktionen. ("Physical Chemistry of Homogeneous and Heterogeneous Gas Reactions"). By Dr. Karl Jellinek. Leipzig: S. Hirzel. 1913. (M. 30).

The object of this monumental work on the physical chemistry of gas reactions is to show what light has been thrown by modern research in physical chemistry on the nature and occurrence of gaseous reactions, and also to illustrate chemical conceptions by reference to experi-

mentally observed facts. The text is divided into four sections. The first and longest deals with the statics of gas reactions; in the theoretical part of this section the references to Planck's work are very numerous, and a thorough exposition is given of the theory of heat radiation. The experimental work which has been done on the subject is very fully described. The second section, on kinetics, is comparatively short, and deals almost entirely with homogeneous reactions, hardly any work having yet been published on heterogeneous reactions. The two last sections of the book deal with the electrochemistry and photochemistry of gas reactions, and give particularly interesting accounts of the research which has been done is the last few years in these branches of physical chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 11, 1913.

1.5.Hexenic Ether Oxides.—R. Dionneau.—Phenoxyhexene, $C_6H_5OC_6H_{11}$, can be obtained by the action of sodium on 1.3.phenoxyiodopropane, $C_6H_5O(CH_2)_3I$. On bromination it yields a dibromide, $C_6H_5OC_6H_{11}Br_2$. Excess of fuming hydriodic acid converts it into diiodohexane, $C_6H_{12}I_2$, while with the gaseous acid it gives phenoxyiodohexane, the magnesium derivative of which with water yields phenoxyhexane. Phenoxyhexene gives phenoxyvalerianic acid on oxidation.

Amino Alcohols.—M. Brenans.—The author has studied the series of amino alcohols prepared by the action of the fatty amines on the products of condensation of epichlorhydrine or dichlorhydrine with the phenols, and has also prepared some glyceric ethers of the phenols homologous with phenoxypropanediol. Aminophenoxypropanediol is specially interesting on account of its physiological action. It contains two very active groups, the amino group and the group $OCH_2.CHOH.CH_2OH$.

Fluorine in Reagents.—P. Carles.—It has been shown that fluorine is a constituent of the ashes of various vegetables, of sea-water, &c., but the author also finds that it is very difficult to obtain certain reagents quite free from fluorine. Thus nitric acid and its salts, baryta, barium acetate, sodium bicarbonate, potassium bicarbonate, ammonium carbonate, &c., always contain appreciable amounts. Hydrochloric and sulphuric acids, on the other hand, are often quite free from fluorine.

Gravimetric Method of Determining Carbonic Acid.—A. Dejeanne.—The CO_2 to be determined is precipitated by a titrated solution of baryta, strontia, or lime. Magnesium chloride solution is added, and thus a compound is obtained which is stable towards the CO_2 of the air. An aliquot part of the solution is separated, and the barium, strontium, or calcium is determined as sulphate, carbonate, or oxalate. Since the strength of the baryta solution was known the amount of CO_2 fixed can be deduced.

New Method of Determining Lactic Acid.—A. Bellet.—To determine lactic acid in complex organic substances the albuminoids are first precipitated by Patein and Dufau's reagent. The filtrate is neutralised, treated with dilute H_2SO_4, mixed with sulphate of sodium and sand, and extracted with anhydrous ether in a Soxhlet's extractor. The lactic acid is then determined as ethyl aldehyde, using the property the latter possesses of reducing an argentic ammonium-sodium solution. The author has devised a special apparatus for dropping the aldehyde into an argentic solution of known strength.

MISCELLANEOUS.

Iron and Steel Institute.—*Brussels Meeting, Sept.* 1—4, 1913.—The Autumn Meeting of the Iron and Steel Institute will be held at the Palais des Academiès, Brussels, on Monday, Tuesday, Wednesday, and Thursday, September 1st to 4th, 1913. The following is the list of Papers that are expected to be submitted:—

Armand Baar (Liége)—"Reinforced Pile Foundations for Blast-furnaces."
Prof. E. D. Campbell and F. D. Haskins (University of Michigan)—"Some Experiments of the Effect of Heat Treatment on the Colorimetric Test for Carbon in a 0·32 Carbon Steel."
Prof. A. Campion and J. M. Ferguson (Glasgow)—"A Method of Preparing Sections of Fractures of Steel for Microscopic Examination."
Baron E. Coppée (Brussels)—"The Manufacture of Coke in Belgium."
General L. Cubillo (Madrid)—"The Manufacture of Armour-piercing Projectiles."
Otto Frick (Beckenham, Kent)—"The Electric Refining of Steel in an Induction Furnace of Special Type."
Emil Gathmann (Baltimore)—"Commercial Production of Sound Steel Ingots."
Gevers-Orban (Liége)—"The Distillation of Tar in Metallurgical Practice."
E. Houbaer (Liége)—"The Use of Coke-oven and Blast-furnace Gases in Metallurgy."
Prof. H. Hubert (University of Liége)—"Present Methods of Testing, with Special Reference to the Work of the International Association for Testing Materials."
Baron E. De Laveleye (Brussels)—"A Historical Survey of the Metallurgy of Iron in Belgium."
F. Rogers (Sheffield)—"So-called 'Crystallisation Through Fatigue.'"
Prof. A. Sauveur (Cambridge University, U.S.A.)—"The Allotropic Transformations of Iron."
Dr. J. E. Stead (Middlesbrough)—"A New Method for the Determination of the Critical Points Ac_1 and Ar_1."
Dr. J. E. Stead (Middlesbrough) and Prof. H. C. H. Carpenter (Manchester)—"The Crystallising Properties of Electro-deposited Iron."
Benjamin Talbot (Middlesbrough)—"Modern Open-hearth Steel Furnaces."
Gustave Trasenster (Ougrée, Belgium)—"The Use of Oxygen in Blast-furnaces."
C. Vattier (Valparaiso)—"Note on the Principal Deposits of Iron Ore in Chili."

Members intending to take part in the discussion of any of the above papers can be supplied with copies a week before the Meeting on application to the Secretary, G. C. Lloyd, 28, Victoria Street, London, S.W.

Solubility of Active Deposit of Radium.—E. Ramstedt.—The rate of solution of the active deposit of radium depends upon the material and the surface of the body upon which it is deposited. Clean polished glass is the best to use for studying the deposit. If the induced activity is deposited on the glass as radium A only half the radium B and C formed can dissolve. On platinum and gold from 60—70 per cent dissolves. Radium C is soluble in hydrochloric, sulphuric, nitric, and acetic acids, less soluble in water, ammonia, and solutions of sodium carbonate, and very slightly soluble in organic liquids. Radium B dissolves more rapidly than radium C in water and in dilute acids, less rapidly than radium C in alkaline solutions, and only very slightly in organic liquids. The rate of solution increases with the temperature, both for radium B and radium C. Radium A is fairly soluble in the above solvents and in organic liquids. Oxygen enormously diminishes the solubility of the active deposit of radium.—*Le Radium*, x., 159.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2804.

MOISTURE IN CLOTH.

By E. G. BRYANT, B.A., B.Sc.

A few weeks ago I was asked to examine some cloth that had been exposed for a short time, not more than an hour, in a shop which had been flooded with water from a fire-engine. The idea was that, during that time, it might have become so damp as to render it liable to mildew; there was no question as to its having been actually wetted. A roll of the cloth was wrapped up in waterproof paper and sent to me, together with a piece of almost identical cloth, bought in the ordinary way of business and similarly protected. Neither piece was opened in the laboratory until all preparations had been made for treating it.

The cloth was a so-called Harris tweed, though from its uniform texture and only very medium roughness and thickness, it was probably machine made. In order to test its degree of moisture I cut out six small pieces weighing from 1 to 2 grms. Three were cut near the edge and three about half-way across the breadth; one pair from the outside of the roll, one pair from about the middle, and the third pair from the innermost layers. A similar pair of samples was cut from the smaller sample which had only been exposed to the ordinary atmosphere of the locality.

Each sample was cut, weighed, and put to dry separately, the remainder of the cloth being protected meanwhile from the atmosphere; the samples were weighed between close-fitting watch-glasses. They were dried for half-an hour at a temperature not above 70° C.; further heating caused no change of weight. The percentage losses of weight were as follows:—

Sample unexposed to water	13·96
	12·78
Outside of roll	12·29
	12·8
Middle of roll	13·8
	13·09
Innermost layer	13·49
	13·25

These seemed extremely high; therefore, in order to ascertain that nothing but water had been lost, the samples were left open in the laboratory till next morning, nine or ten hours. On re-weighing them it was found in every case that the original weight had been regained within at most 5 mgs.; in one instance an actual increase of 3 mgs. was found.

Port Elizabeth is on the sea-coast, and is rather noted for a humid atmosphere. Still it is somewhat surprising to find that an ordinary piece of cloth has here a normal water content of 12 to 14 per cent. Perhaps some of your readers may be interested to compare these results with any obtained in different localities.

Grey Institute,
Port Elizabeth, South Africa.

Catalytic Hydrogenation of Acetylenic γ-Glycols in presence of Palladium Black.—Georges Dupont.—The mechanism of hydrogenation in presence of palladium black is different with different classes of glycols. With fatty glycols the hydrogenation of the alcoholic function acts only on the acetylenic glycol, and the saturated alcohol is not reducible. With the aromatic glycols, on the other hand, the hydrogenation is total, and from diphenyl butanediol, for example, the hydrocarbon can be obtained quantitatively.—*Comptes Rendus*, clvi., No. 21.

THE PRECIPITATION OF GOLD BY MANGANOUS SALTS.*

By A. D. BROKAW.

Some interesting occurrences of gold associated with manganese dioxide led to the suspicion that manganous salts, under certain conditions, might react with solutions of gold salts to bring about a mutual precipitation; the gold in the free state and the manganese as hydrated manganese dioxide. A search for literature on such reactions was without avail, and experiments were undertaken with a view to ascertaining if such a reaction is possible, and if so, under what conditions it can take place. The reaction in question is in a sense the reverse of the series of reactions involved in the well-known "chlorination process" of extracting gold from its ores:—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

and

$$3Cl_2 + 2Au = 2AuCl_3.$$

The reaction is doubtless much more complex than the summary equations, but it will be seen that a reversal of the series would lead to the formation of gold and manganese dioxide.

Auric chloride solutions of varing concentrations were mixed with solutions of manganous chloride with concentrations ranging from 0·5 N up to saturation, but no reaction was detected even when the mixture was boiled for several minutes. The addition of a very small amount of alkali to the mixtures, in the cold, caused an immediate precipitation of a dark brown mass resembling manganese dioxide in the hydrated form commonly precipitated. The precipitate was collected, carefully washed to free it from the gold solution, and then treated with standard oxalic acid, containing a small amount of sulphuric acid. The solution thus obtained was divided into equal portions; one was analysed for manganese and the other titrated for loss of oxalic acid. The results showed that for every equivalent of manganese an equivalent of oxygen had been taken up by the oxalic acid, proving the precipitate to be manganese dioxide. In a check experiment the precipitate was taken into solution with the standard oxalic-sulphuric acid mixture, which was titrated for loss of acid. The manganese in solution was then re-precipitated as hydrated manganese dioxide by a standard method, and the precipitate was again treated with the standard acid mixture. The same loss of acid as before showed the original precipitate to be manganese dioxide.

Gold was left by the solution of oxalic acid, and was readily recognised as such.

Gold chloride solutions are notably acid in their reaction, due probably to hydrolysis in part, and in part to the ionisation of an addition product with water. Hittorf and Salkowsky showed by electrolytic experiments that gold chloride solution is ionised as follows:—

$$\overset{+}{2H} + \overset{=}{AuCl_3O}.$$

Solutions of gold chloride show marked acid properties toward indicators, and apparently the acidity thus developed is sufficient to suppress the reaction

$$2Au^{+++} + 3Mn^{++} = 2Au + Mn^{++++}.$$

If we postulate the intermediate formation of $MnCl_4$ in minimal amounts, we are justified in assuming that the salt would be largely hydrolysed, since tetravalent manganese is a very weak base. This hydrolysis would be suppressed by the presence of acids, but on reducing the acidity hydrolysis might become effective, forming the very slightly soluble hydrated manganese dioxide, and with this removed from the equilibrium system by precipitation, the reaction might proceed until concentrations were diminished to equilibrium conditions.

It is of interest to note that the precipitation began long

* Paper presented at the Milwaukee Meeting of the American Chemical Society, March, 1913. From the *Journal of Industrial and Engineering Chemistry*, v., No. 7.

before the solutions were entirely neutralised, as shown by indicator tests. This was shown in another way by placing a crystal of Iceland spar in the mixture of gold and manganous chlorides in solution. A slight effervescence occurred, and after a few hours the crystal was covered with a brown coat of manganese dioxide in which flakes of gold were plainly visible. The precipitation of gold was practically complete when an excess of $MnCl_2$ was employed, though this solution had at least the acidity of saturated carbonic acid.

An interesting reaction of similar nature was found to take place between auric chloride solution and manganous carbonate. The precipitated carbonate (doubtless amorphous, in part, at least) reacts at once, and is turned to the dark brown hydrated dioxide. The crystallised carbonate, that is, the mineral rhodochrosite, reacts slowly, but, after a day, a crystal was coated with dark brown and flakes of gold were plainly discernible.

Summary.

If we suppose manganese tetrachloride to be an intermediate product, present only in very minute traces, we may find in it some basis of explanation. Suppose—

$$2AuCl_3 + 3MnCl_2 \rightleftarrows 2Au + 3MnCl_4.$$

Since tetravalent maganese is an exceedingly weak base it should be little ionised, but it may be subject to two other sorts of dissociations, namely :—

1. A molecular dissociation, $MnCl_4 = MnCl_2 + Cl_2$.
2. Hydrolytic dissociation,

$$MnCl_4 + 4H_2O = Mn(OH)_4 + 4HCl.$$

Theoretically we should have the hydrolysis constant

$$\frac{Mn(OH)_4 \times (HCl)_4}{MnCl_4} = K,$$

assuming hydrolysis according to the above equation. It is obvious that the presence of acid would tend to cut down the hydrolysis and allow the tetrachloride to become sufficiently concentrated to make its molecular dissociation appreciable—the greater the concentration of acid the greater this tendency—and we may, in this way, easily obtain conditions under which free chlorine is liberated, as in the chlorination process.

If, however, the acid concentration is reduced below a certain figure the concentration of the tetrahydroxide will reach saturation. Any further reduction of acidity must result in the precipitation of the hydrated dioxide. It will be seen that such an adjustment may be very delicate indeed—and this seems to be supported by the lack of success in preparing the tetrachloride, subject, as it would be, to both hydrolytic and molecular dissociation.

THE PYROSULPHATES OF SODIUM AND POTASSIUM AS CONDENSING AGENTS.

By ALLAN F. ODELL and CLEVE W. HINES.

THE availability of the pyrosulphates of sodium and potassium as condensing agents seems never to have been taken advantage of except in the preparation of acrolein from glycerol, and in the preparation of certain alkyl esters of aliphatic and aromatic acids (Bogojawlenski, *Ber.*, 1905, xxxviii., 3344). The ready conversion of these salts into the bisulphates by the addition of water should be the means for their effective application as mediums to abstract water in organic syntheses.

Attention was drawn to this probability when an attempt was made in this laboratory to find a better method for the sulphonation of the mixed alkyl aryl ketones—aceto phenone in particular. This ketone could not be sulphonated satisfactorily by the use of these salts in combination with sulphuric acid. At temperatures up to that of the water-bath, acetophenone yielded triphenylbenzene in varying quantities. The greater part of the acetophenone was recovered, most of the time, unchanged. The same experiments conducted at temperatures from 140° to 200° yielded a large amount of a brittle dark coloured resin. This was probably a decomposition product of the ketone (*Ber.*, vii., 1123).

As a method for the preparation of triphenylbenzene, the experiment carried out at low temperatures is probably more convenient than the usual method of employing hydrochloric acid as a condensing agent (*loc. cit.*).

The most favourable conditions for the formation of triphenylbenzene were determined in the following experiment :—

Twenty-five grms. of acetophenone are mixed with 52 grms. of potassium pyrosulphate, freshly prepared and finely powdered, and about 4 grms. of concentrated sulphuric acid stirred into the mixture. This is then heated in a closed flask in an air-bath to 45° for thirty hours. At the end of this time the solid mass is treated once with 85 per cent alcohol to extract the unchanged acetophenone, then with hot water until the acid sulphate of potassium is dissolved. The residue remaining, when re-crystallised from glacial acetic acid, gives glistening white needles of triphenylbenzene, m. p. 172°. The yield varies from 65 per cent to 85 per cent of the theory.

This particular condensation would not take place with the pyrosulphate alone, even when heated with it in a sealed tube for six hours to 180°. Neither would it take place with sulphuric acid alone.

With the idea of testing the applicability of the pyrosulphates in other condensations, a number of experiments were carried out. The results of these go to show that these salts may be used where a mild condensing agent is required.

The general method employed consisted of mixing the substances to be condensed in the molecular proportions required and adding 1 molecule of the pyrosulphate for each molecule of water to be abstracted. In the examples given below, no solvent was used to bring about the intimate mixture of the reacting substances.

The following cases were thought to be of sufficient value to give the processes in detail :—

Benzal-aniline.—Twenty-one grms. of benzaldehyde, 20 grms. of aniline, and 52 grms. of potassium pyrosulphate are heated on the water-bath for thirty minutes. The resulting solid is treated with ether, whereby the benzal-aniline is extracted and is obtained almost pure on evaporation of the solvent. The yield is almost quantitative.

Benzal-malonic Acid.—Nine grms. of malonic acid, 10 grms. of benzaldehyde, and 28 grms. of pulverised potassium pyrosulphate are mixed and heated in the boiling water-bath for three hours. The resulting mass is treated with 150 cc. of boiling water, heating until everything dissolves, and filtered. On cooling slowly, benzalmalonic acid crystallises out in an almost pure condition, m. p. 192—195°. The yield is about 75 per cent of the theory.

Benzal-acetophenone.—Twelve grms. of acetophenone, 10 grms. of benzaldehyde, and 25 grms. of pulverised sodium pyrosulphate are mixed and heated in the boiling water-bath for six hours. The residue is treated with 75 cc. of water and boiled to dissolve the acid sulphate. The unchanged acetophenone and benzaldehyde form a layer on the top of the resulting solution, from which the benzal-acetophenone crystallises out on standing. The crystals are drained oft and washed with cold water, then with dilute alcohol. The compound so obtained is almost pure, with a melting-point of 57° to 58°. The yield is about 30 per cent of the theory.

Acetanilide.—Thirty grms. of glacial acetic acid, 25 grms. of aniline, and 25 grms. of pulverised sodium pyrosulphate are heated in a flask, with an air condenser, in an oil-bath at 130—140° for one hour. The resulting mass is powdered and boiled with 300 cc. of water until everything dissolves. On cooling, acetanilide of m. p. 113° crystallises out. The yield is almost quantitative.

Efforts to produce condensation between aniline and the phenols were not so successful. Condensation apparently

took place, probably with the formation of sulphuric acid esters (*cf.*, Lassar-Cohen, *Arbeitsmethoden*, pp. 312—3, 4th Aufl.), which were combined with aniline. The products resulting from the crystallisation of the reaction mixture from water, however, consisted chiefly of aniline sulphate. These were not further examined.

When 1 molecule of benzaldehyde is mixed with 1 molecule of resorcinol and 1 molecule of potassium pyrosulphate and heated in the water-bath for twenty minutes, a presumably quantitative yield of an insoluble amorphous canary yellow product results. This contains sulphur, probably as a sulphuric ester also. The compound dissolves readily in potassium hydroxide to a deep red solution, from which it may be reprecipitated on the addition of hydrochloric acid. It does not melt below 300°. This substance will receive more thorough examination at a later date.

As condensing agents, the pyrosulphates would seem to serve excellently in instances analogous to those that have been cited. They have the advantage of being clean and convenient to handle, and do not cause the formation of resinous or tarry products when used alone. This was found to be the case in a large number of experiments which were carried out qualitatively. Furthermore, it is a simple matter to prepare them quickly by fusing the normal sulphates of sodium or potassium with slightly more than the theoretical amount of sulphuric anhydride.

Summary.

The pyrosulphates of sodium and potassium are con venient and effective as mild condensing agents.

Good results were obtained by means of these agents in the preparation of triphenylbenzene, benzal-aniline, benzal-malonic acid, benzal-acetophenone, and acetanilide.

The pyrosulphates cannot be used to condense the phenols with other substances.—*Journal of the American Chemical Society*, xxxv., No. 1.

THE BROMINE AND IODOMETRIC METHODS FOR THE VOLUMETRIC DETERMINATION OF CRESOL.

By C. M. PENCE.

Of the several methods suggested for the volumetric determination of phenol, the bromine method has received the most consideration, and in almost every instance where bromine has been used an attempt has been made to substitute iodine in its stead.

The popularity of the bromine method is no doubt due to two causes. First, to the fact that it answers the demand for a reliable method in the determination of the first member of the series, namely, phenol; second, to the ease in manipulation resulting from the use of the Koppeschaar bromine solution.

Now cresol is the next member of the homologous series; however, it presents upon treatment with bromine solution and acid problems quite different from that of phenol. Since commercial cresol is a mixture of the three isomeric phenols *o*-, *m*-, and *p*-cresol, the presence of the CH_3 group in the different positions necessitates the formation of compounds structurally unlike and empirically the same, and also causes, in the case of meta cresol, the formation of compounds both structurally and empirically different from those formed by *o*- and *p*-cresols. In 2.4.6. tribrom phenol brom, the bromine occupies both the *o* and *p*-positions. Now, in the case of *o*- and *p*-cresol the CH_3 group occupies the *o*- and *p*-positions, and only dibromcresol and dibromcresol brom compounds can be readily formed, since the CH_3 group is more difficult to replace by free Br than is a hydrogen atom. However, the CH_3 group is slowly replaced, and prolonged standing (several days) results in formation of tribromphenol brom. W. Autenrieth and F. Beuttel have recently published the results of an extensive investigation along this line ("Ueber die Bestimmung des Phenols, Salicyl Alkohols, der Salicylsäure und *p*-Oxybenzoësäure als Tribrom Phenol Brom," *Archiv. der Pharm.*, 1910, p. 112).

Meta cresol forms tribrom-*m*-cresol brom, since the CH_3 group is not in the position that the Br atom would occupy.

H. Ditz and F. Cedivoda have proposed a bromine method for cresols depending upon the difference in speed of reactions between bromine and *m*-cresol on the one hand and bromine and *o*- and *p*-cresols on the other ("Reactions of Bromine with Phenol and the Cresols, a Process for Calculating the Composition of Mixtures thereof," *Zeit. Angew. Chem.*, 1899, pp. 873 and 897; Abstr., *Analyst*, xxv., 74). If either *o*- or *p*-cresol is mixed with a known excess of bromine solution, acidified with (1 : 1) hydrochloric acid, and agitated for one minute, on adding KI and titrating with thiosulphate it will be found that each molecule of *o*- and *p*-cresols has absorbed 2 atoms of bromine. Under the same conditions each molecule of *m*-cresol will absorb 3 atoms of bromine. Now, if acidification is effected by concentrated sulphuric acid, the solution shaken for five minutes, and insoluble matter removed by filtration, 3 atoms of bromine will have combined with each molecule of *o*- and *p* cresol, 4 atoms with each molecule of *m*-cresol.

The above method depends for its success upon definitely fixed conditions, namely, time, strength of acid, excess of bromine, &c. F. Russig and G. Fortmann have criticised this method ("Estimation of Cresol," *Zeit. Angew. Chem.*, 1901, p. 157; Abstr. *Journ. Chem. Soc.*, 1901, [2], p. 289), and H. Ditz has replied at length ("Estimation of Cresol," *Zeit. Angew. Chem.*, 1901, p. 160; Abstr. *Journ. Chem. Soc.*, 1901, [2], p. 289).

The present study of the reaction of bromine and iodine upon the different cresols was made for the purpose of finding which of the cresols were amenable to assay by processes which do not require previous knowledge concerning the percentage of product; that is, by processes dependent upon the formation of definitely fixed comparatively stable final products, namely, compounds containing 3 atoms of bromine in combination.

Samples of the individual cresols were re-distilled and volumetric solutions prepared from the distillates, small amounts of N/2 NaOH being added to facilitate solution. Aliquot portions of these solutions were used in the several determinations.

The results appearing in the tables are based upon the formation of dibromcresol brom and tribrom compounds on the one hand and diiodo compounds on the other.

Ortho cresol does not readily form a stable dibrom-*o*-cresol brom or a tribrom compound, as is evidenced in Exp. 1. However, upon one and a-half hours' standing more than sufficient Br is absorbed for the formation of these compounds, and the addition of 10 to 30 cc. of 10 per cent KI with from one and a-half to three and a-half hours' standing does not result in the liberation of the bromine necessary for the formation of either dibrom-*o*-cresol or a tribrom compound, as would occur if reaction proceeded in a manner strictly analogous to phenol (Exps. 2, 3, and 4).

Now, a greater dilution results in the absorption of a smaller quantity of bromine, but results are still too high, Exps. 5 and 6. Increased standing after addition of 20 cc. 20 per cent KI causes a reversal with practically theoretical quantities of bromine absorbed, the time of standing being materially reduced upon increase in the quantity of KI (Exps. 7, 8, 9, and 10).

An increase in concentration of bromine in contact with *o*-cresol, as is effected by larger quantities of Br solution, or a decrease in the quantity of cresol solution, results in the absorption of much more than the theoretical quantity of bromine, and even long standing in contact with increased quantities of KI, suitable reversal does not take place (Exps. 11, 12, 13, 14, and 15).

The effect due to increase in the quantity of acid is very

Ortho Cresol.

No.	Ortho cresol.	N/10 Br.	H_2O.	Conc. HCl.	Time of standing.		20 per cent KI.	Conc. HCl.	Time of standing.		Results.
	Cc.	Cc.	Cc.	Cc.	Hrs.	Mins.	Cc.	Cc.	Hrs.	Mins.	Per cent.
1.	20	50	175	5	0	20	10	—	1	30	94·45
2.	20	50	175	5	1	30	10	—	1	30	103·5
3.	20	50	175	5	1	30	10	—	2	30	102·7
4.	20	50	175	5	1	30	30	—	3	30	101·1
5.	20	50	275	5	1	30	20	—	2	0	100·98
6.	20	59	275	5	1	30	20 (*a*)	—	2	0	100·68
7.	20	50	275	5	1	30	20	—	14	0	99·78
8.	20	50	275	5	1	30	30	—	2	0	99·98
9.	20	50	275	5	1	30	30	—	3	30	100·17
10.	20	50	275	5	1	30	30	—	4	30	99·95
11.	20	75	275	5	1	30	20	—	2	0	109·4
12.	15	50	275	5	1	30	30	—	18	0	105·15
13.	10	50	275	5	1	30	30	—	18	0	106·85
14.	15	50	275	5	3	0	30	—	0	5	113·3
15.	15	50	275	2·5	5	0	30	—	18	0	106·9
16.	10	50	275	2·5	4	0	30	5	20	0	93·4
17.	15	50	275	2·5	5	0	30	5	40	0	86·22

No.	Ortho cresol.	N/10 I.	$CH_3COONa.3H_2O$.	Time of standing.		Procedure.	Result.	Excess N/10 I.
	Cc.	Cc.	Grms.	Hrs.	Mins.		Per cent.	Cc.
18.	25	50	5	0	30	Diluted, added 5 cc. $CHCl_3$, titrated with N/10 thiosulphate, using starch as indicator.	93·66	± 25
19.	25	50	5	1	15		100·04	± 25
20.	25	50	5	14	0		100·71	± 25
21.	25	50	9	1	0		99·93	± 25
22.	25	50	9	2	0		100·1	± 25

(*a*) Heated to 40° C. after addition of KI.

Meta Cresol.

No.	Meta cresol.	N/10 Br	H_2O.	Conc. HCl.	Time of standing.		20 per cent KI.	Conc. HCl	Time of standing.		Result.
	Cc.	Cc.	Cc.	Cc.	Hrs.	Mins.	Cc.	Cc.	Hrs.	Mins.	
1.	20	50	—	5	0	1	10	—	1	0	97·9
2.	20	50	—	5	0	30	10	—	2	0	98·48
3.	20	50	—	5	1	0	10	—	1	0	99·2
4.	20	50	—	5	1	30	10	—	2	0	95·9
5.	20	50	175	5	0	30	10	—	2	0	99·6
6.	20	50	175	5	1	30	10	—	2	0	100·07
7.	20	50	175	5	3	0	10	—	18	0	99 93
8.	20	50	175	5	6	0	40	—	18	0	99·81
9.	15	50	175	5	6	0	10	—	0	5	101·11
10.	15	50	175	5	6	0	10	—	0	30	100·5
11.	15	50	175	5	6	0	10	—	1	30	100·2

No.	Meta cresol.	N/10 I.	$CH_3COONa.3H_2O$.	$NaHCO_3$.	Time of standing.	Procedure.	Result.
	Cc.	Cc.	Grms.	Grms.	Hrs.		Per cent.
12.	25	40	9	—	1	Diluted, added about 5 cc. $CHCl_3$, and titrated with N/10 thiosulphate, using starch indicator.	118·5
13.	25	40	—	0·5	1		122·0
14.	25	40	—	2·0	1		130·0
15.	25	50	—	2·0	2		155.0
16.	25	50	9	—	2		152·0

Para Cresol.

No.	Para cresol.	N/10 Br.	H_2O.	Conc. HCl.	Time of standing.		20 per cent KI.	Conc. HCl.	Time of standing.		Result.
	Cc.	Cc.	Cc.	Cc.	Hrs.	Mins.	Cc.	Cc.	Hrs.	Mins.	Per cent.
1.	20	50	275	5	1	0	10	—	2	0	81·1
2.	20	50	275	5	4	30	10	—	18	0	95·73
3.	20	50	—	5	4	30	10	—	18	0	76·35
4.	15	50	275	2·5	3	0	10	—	0	5	97·34
5.	15	50	275	5	1	30	30	—	18	0	89·72
6.	10	25	200	2·5	3	0	10	—	18	0	101·8
7.	10	25	200	2·5	3	0	20	—	18	0	101·75
8.	10	25	200	5	3	0	10	—	18	0	97·7
9.	10	25	200	2·5	8	30	10	—	16	0	104·6
10.	10	25	200	2·5	4	0	30	5	20	0	84·94
11.	10	25	200	2·5	5	0	30	5	40	0	82·90

No.	Para cresol.	N/10 I.	$CH_3COONa.3H_2O$.	Time of standing.	Procedure.	Result.	Excess.
	Cc.	Cc.	Grms.	Hrs.			Cc.
12.	25	30	9	1	Diluted, added 5 cc. $CHCl_3$, titrated with N/10 thiosulphate using starch as indicator.	98·81	25
13.	25	30	15	1		99·56	25
14.	25	40	9	1		99·75	25
15.	25	50	9	1		99·75	25
16.	25	50	9	2		99·75	25

marked. When bromine is liberated by one-half the usual quantity of concentrated HCl sufficient reversal does not take place after addition of KI (Exps. 14 and 15). However, when an additional 5 cc. of concentrated HCl are added at the same time as the KI, the reversal causes far less than theoretical quantities of bromine to remain in combination (Exps. 16 and 17).

Thus it will be seen that practical results dependent upon the formation of a dibromcresol brom or tribrom compound cannot be obtained except by definitely fixing the several conditions of the experiment in pursuance of which a previous knowledge of the percentage of *o*-cresol is required.

Now, when iodine acts upon *o*-cresol, diiodo-*o*-cresol is formed. The reaction is reversible, and sodium acetate is added to unite with the hydriodic acid produced by the substituting iodine, thereby causing the reaction to proceed to completeness (Exps. 18, 19, 20, 21, and 22). In this case the reaction ends with the formation of diiodo compound, hence it is made the basis of the following method for the determination of *o*-cresol.

Dissolve 2 to 2·5 grms. *o*-cresol in distilled water containing about 10 cc. N/2 NaOH to facilitate solution. Dilute to 1000 cc. Withdraw 25 cc. portions and place in a 500 cc. glass stoppered receptacle. Add to the receptacle approximately 9 grms. sodium acetate, and then 50 cc. N/10 I solution. Let stand one hour, dilute with 100 to 200 cc. distilled water, added a few cc. of $CHCl_3$ to dissolve the precipitated diiodocresol, and titrate with N/10 thiosulphate, using starch as an indicator.

1 cc. N/10 I = 0·002681 grm. *o*-cresol.

Meta cresol does not rapidly form tribrom-*m*-cresol brom with the subsequent formation of tribrom-*m*-cresol upon standing in contact with KI (Exps. 1, 2, and 3). If the *m*-cresol solution stands one and a half hours in contact with the bromine and then 10 cc. 20 per cent KI are added, and solution is allowed to stand one to two hours, all the cresol is converted into tribrom *m*-cresol (Exp. 4).

Dilution permits a more rapid reaction which almost completes itself in half an hour. The addition of KI causes a complete reversal, even though the time of standing in contact with free bromine has been much prolonged (Exps. 5, 6, 7, 8, 9, 10, and 11).

It is thus apparent that *m* cresol may be determined by a conversion into the tribrom compound.

Upon the other hand, when iodine acts upon *m*-cresol in the presence of sodium acetate or sodium bicarbonate, a diiodo compound that may be made the basis of calculation is not produced (E. Richard, "Preparation of Iodo Derivatives of Phenol," *Journ. Pharm. Chem.*, 1902, xv., [5], 217; Abstr. *Journ. Soc. Chem. Ind.*, 1902 p. 423; Messenger and Vortmann, "New Class of Iodated Phenols," *Ber.*, xxii., 2312; Abstr. *Journ. Chem. Soc.*, 1889, p. 1150). More than the theoretical quantity of iodine is absorbed (Exps. 12, 13, 14, 15, and 16).

Para cresol absorbs bromine much more slowly than either of the other cresols. Under similar experimental conditions, four and a-half hours' standing in contact with free bromine results in absorption of only 95·73 per cent of the theoretical quantity (Exps. 1, 2, and 3). If concentration of free bromine is increased and the usual quantity of HCl decreased one-half, the bromine in combination exceeds the amount necessary for the formation of a dibrom-*p*-cresol brom or tribromcresol compound, and eighteen hours' standing does not result in sufficient decomposition even though the quantity of KI is doubled (Exps. 4, 5, 6, 7, 8, and 9).

However, an increase in both HCl and KI results in a most pronounced reversal ("Zur Quantitativen Bestimmung des Phenols auf Parakresols in Gemischen derselben und ihre Anwendung and den Harn," *Pharm. Zentralhalle*, 1911, p. 1288), which is due to the decomposition of dibrom-*p*-cresol brom into dibrom-*p*-cresol (Exps. 10 and 11).

Here, again, the result is directly dependent upon conditions, and previous knowledge is necessary on the part of the operator.

Now, when iodine reacts with *p*-cresol in presence of the condensing agent sodium acetate, diiodo-*p* cresol is formed in theoretical quantity if sufficient time is allowed for reaction to complete itself.

This reaction is made the basis of a method for the determination of *p*-cresol (Exps. 12, 13, 14, 15, and 16). The procedure is exactly the same as that given under *o*-cresol.

Summary.

1. Usual bromine methods for determination of cresol depend upon fixed conditions presupposing a previous knowledge on the part of the operator, and while they may be of service they do not satisfy the demand for a desirable method.

2. Tribrom-*o*- and *p*-cresol brom compounds cannot be formed in a manner analogous to the production of 2.4.6-tribrom phenol brom. Dibromcresol brom compounds are formed, and finally tribromphenol brom; however, *o*- and *p*-cresols cannot be determined volumetrically by a conversion into these compounds.

3. Meta cresol is determined by a conversion into tribrom-*m*-cresol.

4. Ortho and para cresols form diiodo compounds, and this reaction is made the basis of a method for their determination.

5. Meta cresol does not yield diiodo compounds under the same conditions; hence, cresol U.S.P. or any mixture containing *m*-cresol cannot be determined by a volumetric iodine method.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS.*

By YOSHITO YAMAUCHI.

Several workers, among whom we may mention Schönbein, Williamson, Maquenne, and Mailfert, have studied the oxidation of certain inorganic salts by ozone, but report, for the most part, only the final products of the reactions and not the way in which the ozone has acted to bring them into existence. The author has therefore, at the suggestion of Prof. M. Chikashige, sought to get more accurate information upon this point, and presents the following as a brief account of his investigation:—

I. *Method of Investigation.*

Estimation of the Ozone which is to be used for Oxidation.—To determine the concentration of ozonised oxygen before consuming it, there has existed only one method, that of directly weighing a certain known volume of it and of comparing this weight with that of an equal amount of pure oxygen. Since this method is by no means convenient, the author contrived a new one, that of filling two large cylindrical glass tubes of known volumes with one and the same sample of ozone, so that he could use one for the purpose of estimation and the other for the oxidation.

Take two tubes, A and B, of nearly equal capacity, 35 cm. in length, and about 5 cm. in diameter. They are provided with glass cocks, *a* and *a'*, at one end, and with double cocks, *b* and *c* and *b'* and *c'*, at the other. They are mounted in a somewhat slanting position, and connected with a bent tube at the lower end. Fig. 1 represents the arrangement. Keeping now all the cocks open, ozonised oxygen is passed first from A to B, then from B to A, the amount of the gas passed each time being almost 1·5 times more than the total volume of the two tubes. Working regularly in this manner it was always found that the amount of ozone in both tubes stood almost in a constant ratio, as will be seen below.

* *American Chemical Journal*, xlix., No. 1.

Comparison of the Amount of Ozone in the Two Tubes.—After having filled the tubes with ozonised oxygen, close all the cocks except *c* and *c'*, and disconnect the tubes. Take then two aliquot portions of a neutral potassium iodide solution, and pour them each into two different beakers, from which transfer them separately into the spaces between *b* and *c*, and *b'* and *c'*, respectively. Then, shutting off the cocks *c* and *c'* and opening the others, *b* and *b'*, let the solutions into the cylindrical parts of the tubes, and shake vigorously until they no longer give the odour of ozone. The solutions now containing liberated iodine are thoroughly washed down into their original vessels, and, after being acidified with a few drops of dilute sulphuric acid, are titrated for iodine by means of a standard solution of sodium thiosulphate (*cf.* Treadwell and Anneler, *Zeit. Anorg. Chem.*, 1906, xlviii., 87). The amounts of the ozone corresponding to these quantities are calculated from the well established equation :—

$$O_3 + 2KI = K_2O + O_2 + I_2 \quad . \quad . \quad . \quad . \quad 1.$$

The amount of ozone thus found in the two tubes is compared after being re-calculated on the basis of a litre volume and the mean ratio taken from six such determinations, as will be seen in Table I.

Now, by the aid of this, we can easily calculate the amount of ozone in one tube, upon actually finding that in the other.

Manner of Ozone Decomposition during the Process of Oxidation.—Taking a known amount of ozone, the author caused it to act upon a salt in solution, whose amount was known and was greater than one equivalent as compared with the ozone used. When the reaction was over, he estimated the amount of the oxidised salt, from which, by taking account of the amount of ozone used, he could directly infer how the oxone decomposed before the oxidation ; whether as—

$$O_3 = O_2 + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 2,$$

where only one-third the oxygen atoms would have entered into the reactions, or as—

$$O_3 = 3O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 3,$$

where all three atoms would have taken part in the oxidation. With the aid of such inferences, he established chemical equations to represent the oxidising action of ozone according to the various cases.

Table I.

No.	Ozone in grm. Per 671 cc. (Tube A).	Ozone in grm. Per litre (*a*).	Ozone in grm. Per 693 cc. (Tube B).	Ozone in grm. Per litre (*b*).	*a*/*b*.
1 ..	0·0058	0·0087	0·0062	0·0089	0·98
2 ..	0·0053	0·0080	0·0058	0·0083	0·96
3 ..	0·0048	0·0071	0·0044	0·0064	1·11
4 ..	0·0081	0·0120	0·0087	0·0126	0·95
5 ..	0·0032	0·0048	0·0032	0·0046	1·04
6 ..	0·0147	0·0219	0·0151	0·0217	1·01
			Mean		1·01

II. *Reactions of Ozone Investigated according to this Method.*

1. *Arseniaus Acid.*—That metallic arsenic is oxidised by ozone finally to arsenic acid was first made known by Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 288). The determination of ozone by the use of arsenious acid is based on this reaction (Thénard, *Comptes Rendus*, lxxv., 174 ; Hartley, *Journ. Chem. Soc.*, 1881, xxxix., 120 ; Treadwell and Anneler, *Zeit. Anorg. Chem.*, 1906, xlviii., 94).

The author took a known amount of ozone contained in a cylindrical tube, let in an aliquot portion of a neutral potassium arsenite solution, and allowed the mixture to react for about half-an hour, the quantity of the oxidised salt being then calculated from the amount of the unchanged arsenite, as determined by the use of a standard iodine solution. The ratio of the ozone to the arsenite oxidised is given in Table II.

Table II.

No.	Ozone, in grm.	Arsenious acid oxidised by the ozone, in grm.	Arsenious acid per grm ozone, in grms.
1 ..	0·0093	0·0204	2·19
2 ..	0·0080	0·0149	1·86
3 ..	0·0059	0·0138	2·34
4 ..	0·0116	0·0243	2·10
5 ..	0·0098	0·0215	2·19
		Mean	1 : 2·14

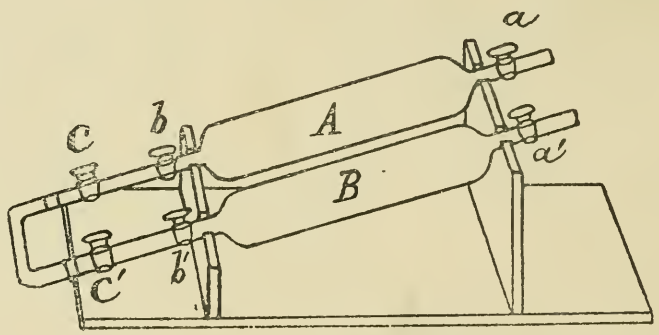


Fig. I.

This reaction is therefore well represented by the usual equation—

$$As_2O_3 + 2O_3 = As_2O_5 + 2O_2 \quad . \quad . \quad . \quad . \quad 4,$$

as it requires 2·06 grms. arsenious oxide per grm. ozone.

2. *Stannous Chloride.*—The conversion of a stannous into a stannic salt by ozone has been studied by Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 293) and Williamson (*Ibid.*, 1847, lxi., 14). If the reaction is, as in other cases,—

$$3SnCl_2 + 6HCl + 3O_3 = 3SnCl_4 + 3H_2O + 3O_2 \quad . \quad 5,$$

the amount of the stannous chloride oxidised by ozone would be in the ratio of 3·96 grms. to 1 grm. of the latter. But if the reaction takes place as follows :—

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O \quad . \quad . \quad 6,$$

the ratio would be 11·87 grms. stannous chloride to 1 grm. ozone ; besides, the pressure in the reaction tube would be then very much reduced, since oxygen is no longer produced in a volume equal to the ozone consumed.

According to the author's experiments the reaction seems to proceed exactly as shown in Equation 6, and not as in 5. After a known quantity of a stannous chloride solution in hydrochloric acid had been mixed in the usual manner with a known quantity of ozone, and left for about half-an-hour with constant shaking, the amount of the stannous chloride entering into reaction was calculated from the amount of the unoxidised salt, which was found

by the use of a standard iodine solution, subtracted from the total amount of the salt taken. The results of the experiments are given in Table III.

TABLE III.

No.	Ozone, in grm.	Stannous chloride oxidised by the ozone, in grm.	Stannous chloride per grm. ozone, in grms.
1 ..	0·0077	0·1147	14·89
2 ..	0·0119	0·1550	13·03
3 ..	0·0089	0·1392	15·64
		Mean	1 : 14·52

This ratio nearly coincides with that calculated from Equation 6. That it is a little more than the latter is due, perhaps, to the simultaneous action of the co-existing ordinary oxygen. It must, however, not be forgotten that what causes the reaction for the main part is the ozone and not the oxygen, because the reaction goes on very rapidly only at first, and as soon as the ozone is used up, the reaction becomes notably slower. Thus the two tubes, A and B, were equally filled with ozone, and treated with equal quantities of a stannous chloride solution. One of the tubes was then left for only twenty minutes, and the other for a much longer interval of time. The oxidation stopped after a certain lapse of time; the degrees of oxidation in both tubes, expressed in terms of the stannous chloride, were nearly the same in spite of so great a difference in time. The results of four such experiments are given in Table IV.

TABLE IV.

Time, in minutes.	Degrees of oxidation in terms of stannous chloride.	*t*/*t*.
20	0·1368	1/1·07
140	0·1468	
20	0·2015	1/1·05
100	0·2120	
20	0·1795	1/1·15
60	0·2062	
20	0·2255	1/0·95
40	0·2133	
	Mean	1 : 1·06

Hence, we have here a new instance of oxidation by ozone, in which the latter acts by decomposing itself according to Equation 3.

3. *Sodium Thiosulphate.*—The action of ozone on sodium thiosulphate seems not to have been studied hitherto by any chemist. When a solution of this salt is shaken with ozone, it becomes milky through the separation of sulphur, while the solution, which remains quite neutral during the reaction, contains sulphite and sulphate, besides some unchanged thiosulphate.

Whether or not a part of the sulphite and sulphate comes from the oxidation of the precipitated sulphur by ozone cannot yet be definitely decided, because sulphur is oxidisable, according to Mailfert (*Comptes Rendus*, 1882, xciv., 1186), while according to Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 282) it is not. With regard to the author's experiment, in which he passed ozone a long time through the precipitated sulphur with neutral reaction suspended in water, he could find only an almost insignificant quantity of sulphite formed. However, in order to make the problem as simple as possible he did not take into account the presence of sulphite from such a source.

Then the quantitative estimation of the reactions was effected in the following manner:—

As usual, a known amount of a sodium thiosulphate solution was introduced into the tube containing a known amount of ozone, and the mixture was allowed to stand for about half-an-hour with frequent shaking. After being separated from the precipitated sulphur, the solution was then examined for its iodine equivalent (6, V.); the latter covers the amount of both the thiosulphate in excess and sulphite. Barium chloride was added to this solution, precipitating all the sulphates, a part of which had been originally present through the oxidation of the thiosulphate by ozone, and the rest derived from the sulphite oxidised by iodine. The amount of the sulphates (1, V.) therefore corresponded to the total weight of the thiosulphate entering into reaction (2, V.) with a definite volume of ozone (*cf.*, Equation 9). Then from the excess (4, V.) of the thiosulphate originally taken (3, V.) over that actually entering into reaction (2, V.), may be directly calculated its iodine equivalent (5, V.), and the difference (7, V.) between this value and that determined before (6, V.), which is a little greater, gives exactly the amount of the sulphite, the amount of the thiosulphate corresponding to it being then calculated from it (8, V.). The amount of the thiosulphate changing into the sulphate (9, V.) can be also calculated by taking the difference of the above quantity from the total amount of the thiosulphate entering into the reaction (2, V.). The ratio of the thiosulphate changing either into the sulphite or into the sulphate becomes nearly 1 : 2 from the mean of four such experiments, as will be seen from Table V.

TABLE V.

No.	Description.	I.	II.	III.	IV.
1.	Barium sulphate found	0·0733	0·1244	0·0826	0·1024
2.	Sodium thiosulphate entering into reaction (calc. from 1)	0·0496	0·0843	0·0560	0·0694
3.	Sodium thiosulphate originally taken (found)	0·1606	0·1606	0·1606	0·1606
4.	Excess of sodium thiosulphate escaping the reaction (diff. between 3 and 2)	0·1110	0·0763	0·1046	0·0912
5.	Iodine equivalent to the above salt (calc.)	0·0891	0·0613	0·0840	0·0732
6.	Iodine equivalent to the thiosulphate solution soon after the reaction with ozone (found) ..	0·1146	0·1142	0·1144	0·1148
7.	Difference between 5 and 6	0·0255	0·0529	0·0304	0·0416
8.	Sodium thiosulphate changing into the sulphite (*a*) (calc. from 7)	0·0159	0·0329	0·0190	0·0259
9.	Sodium thiosulphate changing into the sulphate (diff. between 2 and 8)	0·0337	0·0514	0·0370	0·0435
10.	Ratio of 8 to 9	1 : 2·1	1 : 1·6	1 : 2·0	1 : 1·7

Mean, 1 : 2.

(*a*) From the equation $2I + Na_2SO_3 \cdot H_2O = 2HI + Na_2SO_4$ we see that two atoms of iodine are equivalent to to 1 molecule of sodium sulphite, which is now in its turn equivalent to 1 molecule of sodium thiosulphate.

Hence we find that 2 molecules of sodium sulphate are always produced together with 1 molecule sodium sulphite. Perhaps we have no other way of understanding this reaction than by supposing it to take place in two successive stages. The first is the catalytic decomposition of the thiosulphate into sulphite and sulphur, where the ozone effects no oxidation at all; thus—

$$3Na_2S_2O_3 = 3Na_2SO_3 + 3S \quad . \quad . \quad . \quad . \quad 7.$$

Then follows the second stage, in which only two out of the 3 molecules of sodium sulphite are acted upon by ozone, so that the reaction may be expressed as follows:—

$$2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2 \quad . \quad . \quad . \quad 8.$$

Since we know the amount of ozone necessary to effect the oxidation of thiosulphate, as shown in (9, V.), into

sulphate, we can calculate the amount of the oxidised thiosulphate per grm. ozone, thus :—

TABLE VI.

No.	Ozone, in grm.	Sodium thiosulphate changed into the sulphate, in grm.	Sodium thiosulphate per grm. ozone, in grms.
1 ..	0·0101	0·0337	3·34
2 ..	0·0173	0·0514	2·97
3 ..	0·0111	0·0370	3·33
4 ..	0·0139	0·0435	3·13
Mean			1 : 3·19

Calculated for 1 molecule sodium thiosulphate per molecules ozone, as may be deduced from Equation 8, we have the ratio 1 : 3·29, which is really in good accord with the experimental ratio.

Combining now the two Equations 7 and 8, we establish the following to account approximately for the whole course of the reaction of ozone with sodium thiosulphate :—

$$3Na_2S_2O_3 + 2O_3 = 2Na_2SO_4 + Na_2SO_3 + 2O_2 + 3S \quad . \quad 9.$$

(To be continued).

IMPROVING THE QUALITY OF ALUMINIUM.

ALUMINIUM is a very useful metal, although it is so comparatively new to us ; but like other metals it has its faults, which we seek to neutralise by alloying it with other materials, since the action of heat upon it does not effect any desirable changes therein, as is the case with steel.

Among the experiments that have been made in the way of alloying are those with cobalt, the results of which have not become very generally known, and which are especially interesting when the action of this alloy is increased by the addition of tungsten and molybdenum.

Scientific researches into the chemical relation of aluminium and cobalt in alloy form go to show that those two metals are so to say soluble in each other. Of the various alloys that have been made and studied, the one with the least percentage of cobalt had one-third of this metal therein ; its solidifying point being somewhat above 100° C. Between this compound and aluminium there is a "eutectic" containing only 0·5 per cent of cobalt and having a melting-point lower than that of pure aluminium. There is also in the curve showing the melting-points of the aluminium-cobalt alloys a decided kink at the point corresponding to 20 per cent of cobalt.

With 9 to 12 per cent of cobalt there are obtained alloys that are almost free from bubbles, although the fracture is somewhat coarse and crystalline ; and although the tensile strength is not much above that of pure aluminium the alloy is more readily turned and polished, &c., and much more resistant to atmospheric influences. These alloys are still quite light and much more workable than pure aluminium. The lack of tensile strength is due to the coarse crystalline fracture, but this may be improved by the addition of tungsten (which the Germans call "wolfram") and molybdenum, so that by the help of these an alloy with but a small percentage of cobalt has three times the tensile strength of aluminium, and is also malleable and ductile. These alloys run about 0·8 to 1·2 per cent tungsten, 8 to 10 per cent cobalt, the rest aluminium.

The more cobalt these alloys contain, the less readily can they be rolled, but the greater their tensile strength ; so that those with high cobalt percentage are better for castings, the poorer ones better for forging and rolling. The alloys of molybdenum, cobalt, and aluminium run from 0·6 to 1 per cent molybdenum, 9 to 10 per cent cobalt, the rest aluminium ; these follow about the same general rules as those of wolfram, cobalt, and aluminium, except in the matter of hardness, in which they are inferior to the corresponding tungsten-cobalt alloys.—*Chemical Engineer*, xviii., No. 5. (From *Metal Industry*.)

ANALYSIS OF MILK AND MILK PRODUCTS.*

THE methods employed for the analysis of milk and milk products are, in the main, those published and recommended by the United States Department of Agriculture. In the case of some of the determinations, however, it has been found that the desired information may be obtained through simpler and more rapid procedures than those of the official methods.

The following determinations are regularly made :—Total solids, ash, fat, casein, lactose, and number of bacteria per cubic centimetre.

The Determination of Total Solids.—A sample of about 5 grms. is weighed into a flat aluminium dish and evaporated to constant weight in a water-jacketed air-bath heated to boiling temperature. The final weighing must be made very rapidly to avoid absorption of water from the air.

Ash.—About 20 grms. of samples are weighed into a tared platinum dish, 6 cc. of nitric acid (sp. gr. 1·42) added, and the whole evaporated to dryness on the water-bath. The residue is finally ignited at the lowest possible temperature in an electrically heated muffle until the carbon is completely burned out, leaving a white ash. The whole is then cooled in a desiccator and weighed.

Total Nitrogenous Matter.—A combination of the official Kjeldahl and Gunning methods is used, for which the following reagents are required :—

1. An accurately standardised solution of hydrochloric acid, of about tenth normal strength. This should be standardised by precipitation of the chlorine as silver chloride, which is weighed in a Gooch crucible.

2. A standard alkali solution (NaOH) whose value in terms of the above acid is accurately known. It is convenient to have these solutions exactly equivalent to each other.

In all titrations cochineal is recommended as an indicator. It is prepared as follows :—3 grms. pulverised cochineal is extracted for several days, with frequent shakings, with a mixture of 50 cc. alcohol and 200 cc. distilled water, and the whole filtered.

Pure sulphuric acid, sp. gr. 1·84, a saturated solution of NaOH, a solution of potassium sulphide, 40 grms. per litre, powdered potassium sulphate, pure mercury, and some small lumps of pumice stone are also required.

Upon these reagents blank determinations should be made to make sure that all are nitrogen free, or to provide a constant correction.

Procedure.—A 5 grm. sample of milk is placed in the Kjeldahl digestion flask (used also for the distillation), where it is mixed with 10 grms. K_2SO_4 and 0·66 grm. of mercury, and 25 cc. of conc. H_2SO_4 added. The mixture is heated gently until frothing ceases, and then digested at the full heat of the naked Bunsen flame until colourless or nearly so, and a short time after that point is reached. This should require less than two hours, a much shorter time than either of the official methods.

When the digestion is complete, the flask and contents are allowed to cool, and the solution diluted to 200 cc., a few pieces of pumice being added to prevent bumping and 25 cc. of K_2S solution to precipitate the mercury. The acid is then neutralised and the ammonia liberated by the addition of 60 cc. of the strong alkali solution, the solution being poured down the side of the inclined flask so that it may not mix with the acid solution. The flask is connected with the block tin condenser by means of a bulb tube to prevent any of the alkali solution from being carried over mechanically, and the end of the delivery tube of the condenser placed under the surface of 40 cc. of the N/10 acid in an Erlenmeyer flask. When all is ready, the distillation flask is rotated to mix the solutions, and heat applied. The whole is boiled briskly until about 150 cc. of distillate has passed over, this being sufficient to

* Method of analysis used in the laboratories of the Armour Institute of Technology. From the *Chemical Engineer*, xviii., No. 1.

assure the elimination of all ammonia. At this point the delivery tube is disconnected, the flask removed, and its contents titrated with the standard alkali. The net volume of acid solution times the factor gives net volume of N/10 acid which is equal to vol. of N/10 NH_3 and of N/10 nitrogen which has a strength of 1 cc. = 0·0014 grm.,

so $$\frac{\text{cc. N/10 acid used} \times 0{\cdot}0014}{\text{Wt. sample}} \times 100 = \text{per cent N.}$$

Per cent nitrogen × 6·38 = per cent nitrogenous compounds.

It is frequently desirable to determine pure casein as well as total nitrogenous substances. Casein may be determined in the following way :—

1. A sample of 10 grms. of the fresh milk is made up to 100 cc. with water at 40° to 42° C. in a beaker. To this is added at once 1·5 cc. of a 10 per cent solution of acetic acid. The solution is stirred and allowed to stand for from three to five minutes, when it is decanted through a filter, the precipitate washed several times by decantation, using cold water, and finally transferred to the filter and the washing completed. The precipitated case in may run through the filter at first. In this case, the filtrate should be returned to the filter until it is perfectly clear. The precipitate obtained is run for nitrogen by the method described for total nitrogen.

Per cent nitrogen × 6·38 = per cent casein.

The difference between the total nitrogenous material and the casein is approximely equal to the albumen.

Fat.—For this determination two methods are given :—

1. The Babcock method.
2. A gravimetric method.

1. The Babcock fat test requires a special apparatus, consisting of a centrifuge capable of about 1000 revolutions per minute, and properly graduated bottles and pipettes.

A sample of 17·6 cc. of the thoroughly mixed sample of milk is pipetted into the test bottle and 17·6 cc. of commercial H_2SO_4 (sp. gr. 1·82—1·83) added. After mixing the solution is whirled in the centrifuge for four minutes. Hot water is added up to the neck of the bottle and the bottle whirled for one minute, and finally boiling water again added until the layer of fat comes within the scale, and the whole again whirled for one minute. The readings on the scale give per cent of fat direct.

2. The gravimetric method for fat is carried out as follows :—

A paper coil is prepared by rolling strips of thick filter paper, 2·5 by 25 inches, into solid rolls. Such paper coils may also be purchased prepared for use. They should be thoroughly extracted with ether before use.

About 6 - 8 grms. of milk is weighed in a weighing bottle, and about 5 cc. of this absorbed into the paper coil, care being taken to keep one end of the same dry. A second weighing of the bottle and the milk remaining gives the weight of the sample, which should be about 5 grms. The sample is dried thoroughly in a water-jacketed air-bath, and is then extracted in a Soxhlet or similar type of extraction apparatus for several hours with petroleum ether. After 6 hours the ether is evaporated off and the fat weighed.

Lactose.—The determination of lactose or milk sugar is most conveniently made by means of the polariscope, such as is used in sugar analysis, and which reads percentage of cane-sugar direct. Lacking such an instrument, the gravimetric method is satisfactory, though somewhat longer.

1. *Optical Method.*—For this a sugar polariscope or saccharimeter is employed, whose normal weight for sucrose is 26·048 grms.

By using a constant, exact weight of sample based upon the specific rotary power of pure lactose, it is possible to make the polariscope read percentage direct.

To get the exact weight, it is best to determine the specific gravity of the milk, either by the Westphal balance or by a delicate hydrometer, and then measuring accurately the volume corresponding to the sp. gr. in the appended table :—

Table for instrument whose normal weight for sucrose is 26·048 grms. :—

Sp. gr.	Volume of milk, cc.
1·024	64·30
1·026	64·40
1·028	64·15
1·030	64·00
1·032	63·90
1·034	63·8
1·035	63·7

The volume indicated from the table is run into the flask that corresponds to the instrument in its graduation, and to it is added 30 cc. of a mercuric iodide solution (33·2 grm. KI, 13·5 grms. $HgCl_2$, and 20 cc. glacial acetic acid dissolved in 640 cc. of water), the whole made up to the mark of the flask and mixed thoroughly. It is then filtered through a dry filter, a portion put into the polariscope tube and the readings made.

100 mm. tube reads per cent direct.

200 mm. tube reading is divided by 2.

400 mm. tube reading is divided by 4.

2. *Gravimetric Method.* This depends upon the reducing action of lactose upon alkaline copper tartrate solutions, the weight of Cu_2O formed being a function of the weight of lactose present. Tables of weights of sugars corresponding to given weights of Cu_2O may be found in any of the works upon sugar analysis, food analysis, and kindred subjects.

The solutions used is Soxhlet's modification of Fehling's solution, made as follows :—

1. $CuSO_4 \cdot 5H_2O$, 34·639 grms. dissolved in water and made up to 500 cc.

2. $KNaC_4H_4O_6$ (Rochelle salts), 173 grms. and sodium hydroxide 50 grms. made up to 500 cc.

These solutions are mixed volume for volume just before use.

3. A half normal solution of NaOH.

25 cc. of milk are diluted with 400 cc. of water, 10 cc. of above described copper sulphate solution and 8·8 cc. of the half normal sodium hydroxide solution added. The mixture must be acid at the point and still contain copper in solution. The whole is then diluted to exactly 500 cc., mixed thoroughly, and filtered through a dry paper.

Lactose is now determined upon aliquot parts of this solution as follows :—

Fifty cc. of the mixed copper reagent (half-and-half of copper sulphate and Rochelle salts solutions) are heated to boiling, 100 cc. of the prepared sugar solution added, and the whole boiled for six minutes. The red precipitate of Cu_2O is thrown on a tared Gooch crucible, washed with hot water, then with alcohol, finally with ether, and dried to constant weight at 100°C. Weight $Cu_2O \times 0{\cdot}8883$ = weight Cu.

From the weight in mgrms. of Cu, the corresponding weight of lactose is taken from the table, which may be found in any work upon commercial organic analysis, food analysis, or from *Bull.* 107, U.S. Department of Agriculture.

$$\frac{25 \text{ cc.} \times \text{sp. gr.}}{5} = \text{weight sample of milk.}$$

$$\frac{\text{Wt. of lactose (from table)}}{\text{Wt. sample}} \times 100 = \text{per cent lactose.}$$

Bacterial Count. No milk analysis is complete without a count of the bacteria. For this purpose 1 cc. of the sample is measured into a sterile flask with a sterile pipette, and diluted to 500 cc. with sterile water. One cc. of this solution is taken in a fresh pipette and again diluted to 100 cc.

Six tubes of nutrient agar are placed in hot water, the agar melted, and then allowed to cool to 40° C.

One cc. of the low dilution is placed in each of three

sterile Petri dishes, properly marked. Three samples of the high dilution are similarly prepared. The agar from the tubes is then poured into the dishes, care being taken to allow as little exposure to the air as possible, and the solution and agar mixed by gently flowing the contents of the dish back and forth. The agar is allowed to set and the dishes are then inverted and incubated at a temperature of 38° C. for twenty-four hours, when the number of colonies is counted in each.

Average of counts for the first dilution multiplied by 500 gives bacteria per cc. of the original milk, and for the second dilution the number of colonies is multiplied by 50,000.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Notes on Henri Poincaré.

Prof. Paul Appel, Dean of the Faculty of Science, has just published a notice on Henri Poincaré in the *Scientific Bulletin* of the University of Paris. Poincaré, says Prof. Appel, studied at the Lycée or Public School of Nancy. He was an excellent pupil, whose intelligence, sagacity, and instructive mind were at an early age remarked by his masters. He passed the examination for the degree of Bachelor of Arts on August 5th, 1871, with the note "good." He was received Bachelor of Science on November 7th, 1871.

M. Floquet, the present Dean of the Faculty of Science of Nancy, has communicated the official report of this examination to M. Appel. In this report it is seen that Henri Poincaré obtained to note 0 for the written composition of physics and the note 2 (out of a maximum of 5 points) for the written composition of mathematics. Undoubtedly, says M. Appel, this 0 and this 2 will be noticed a little maliciously. The eminent physicist, mathematician, and philosopher, Henri Poincaré, was, indeed not very brilliant in his examinations. The fact is not of a nature to diminish our scepticism concerning the examination for the Bachelor's degree.

At the end of 1873 Poincaré won the first prize for mathematics at the general competition of all the Parisian Boys' Colleges; he was received first at the competitive examinations for the entry to the Polytechnic School, and fifth for the Higher Normal School. This last fact, joined to the plucking of Galois, the young French mathematician, who died at the early age of 24 years, and who failed to pass the entry examination to the Polytechnic School, was also not of a nature to diminish the scepticism of the learned men concerning competitive examinations — artificial proofs whose results are often belied in after life.

Action of Chloride of Calcium in the Curdling of Milk.

M. Luidet has studied the action of chloride of calcium in the curdling of raw and of cooked milk. He shows that the caseines solubilised by the elements of the serum phosphates, citrates, alkaline chlorides, lactoses, &c., lose their solubility when under the influence of chloride of calcium, the alkaline phosphates are transformed into insoluble phosphate of calcium, and the alkaline citrates are changed into citrate of calcium, in which the caseines are insoluble. Moreover, the bicalcic phosphate that is formed is dissociated in the midst of the water into tricalcic and monocalcic phosphate. This latter attacks the lime which was dissolved by the caseines and makes them more soluble, reforms some bicalcic phosphate which is dissociated in its turn, and so on until all the lime is transformed into insoluble phosphate, which is found again on the curd. The addition of chloride of calcium increases thus the quantity of curds, at the expense of the solubilised caseines in the serum, and augments the tenor of this latter in phosphate of calcium; the chloride of calcium, if too much has not been put in, will disappear, and in the curds there will only be found chloride of sodium and phosphate of calcium, which are the normal elements of cheese.

Dangers of Fire from Incandescent Lamps.

Concerning the burning of the theatre of Stettin, M. Boje has been requested to examine if the cause of the fire might not be attributed to portable electric lamps. To this intent he supplied each type of protector with lamps with carbon filaments of 16 candles, 220 volts, and by turns wrapped them in stuffs of cloth, wool, silk, and linen, so as to isolate them as much as possible from the air. A glass tube plunged in the mass rendered it possible to follow the variations of temperature in the neighbourhood of the lamp. In the case of two lamps the cloth stuff caught fire after twenty-five minutes contact with the ampullas, and after thirty minutes without touching the glass. The light woollen, silk, and cotton stuff took fire when in contact with the bulbs at the end of five to fifteen minutes. The heating was such that the ampulla itself became softened and broke. The two other lamps wrapped up in towels caused burns at the end of thirty minutes and two hours and forty minutes. The highest temperature noted was 213° C.

One lamp was experimented upon by enclosing it in a box with wooden shavings. These took fire at the end of three hours. This experiment demonstrates clearly that all portable lamps actually in use may become dangerous when they are furnished with ampulla with carbon filaments of 16 candles, 220 volts. As a counter-proof, the author has made the same trials with the same envelopes, but supplied with ampullas with metallic filaments of 16 and 50 candles. The combustion was still possible with the ampullas of 50, 32, and 25 candles; only the lamp with a metallic filament of 16 candles was unable in any case to bring about combustion. The highest temperature noted (149° C.) was observed with the No. 1 covering, and the lowest 100° with covering No. 4.

The Lighting of Paris.

"Light, light," cried Goethe when dying, and this cry uttered by the great poet on his dying bed seems to have been heard by the succeeding generations of nearly a century past. Never was the love of light so great as it has been during the last few years. After the still somewhat weak light of the fishtail burners, the electric lamp with carbon filaments made its appearance. It was considered as a great progress. But the systems of lighting were improved. The Auer mantles were a new triumph for gas lighting. The electric lamps with metallic filaments came next, and the struggle between gas and electricity continues interminably.

The lighting of the public streets has followed the progress of private lighting. At the present time the City of Paris is experimenting on two processes of lighting; one electric, the other based on the employment of compressed ges. In the Avenue de l'Opéra, lamps with staples invented by the French engineer Bardon, throw out floods of light. The carbons are replaced by electrodes of steel or made of crystallised substances. On the Place de la République and the Boulevard Raspail there are powerful lamps furnished with mantles and fed by gas under pressure. A quite recent statistic, drawn up by M. Lauriol, chief engineer of the lighting service of Paris, shows that the lighting power of the apparatus which are used for public lighting amounts to about 7,000,000 candles per twenty-four hours. The quantity of gas employed in twenty-four hours for public lighting exceeds 91,600 cubic metres. For the private service the consumption (lighting and force) amounts to 1,140,000 cubic metres. The quantities of electricity employed in twenty-four hours is 13,000 kilowatts for public lighting and 154,000 kilowatts for private lighting. The hours of most intense lighting vary according to the season. It is, however, noticed that the maximum consumption of electricity takes place about 6 o'clock in winter. The maximum consumption of gas takes place about 8 o'clock in summer.

Besides these figures enormous quantities of electricity are consumed by manufactories who produce their own currents, as well as that consumed by companies of public transport, such as the Metropolitan Underground Railway, the lines of electric tramways, and also the large stores who have their own electric installations, &c.

NOTICES OF BOOKS.

Treatise on General and Industrial Organic Chemistry. By Dr. ETTORE MOLINARI. Translated from the Second and Enlarged Italian Edition by THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C. London: J. and A. Churchill. 1913.

BOTH theoretical organic chemistry and its industrial applications are treated in this book, which is a first-rate work of reference for the technical student. The economic aspects of the subject are taken into consideration, and practical ideas as to cost of production, &c., are constantly put before the student. Discrepancies between practice and theory are carefully pointed out, and the conclusions which the author has drawn relating to some disputed points are clearly stated. Metric weights and measures have been preserved in the translation, but prices are given in English currency. It is perhaps rather invidious, in view of the general excellence of the work, to point out that the use of small print and of very copious footnotes makes the reading of the book rather fatiguing, and in some cases, while the meaning is clear the translation is awkward, as, for example, in "Drink causes the direct or indirect death of about 45,000 people.

Petroleum. By Sir BOVERTON REDWOOD, Bart., D.Sc., F.R.S.E., Assoc.Inst.C.E., F.I.C. Third Edition. London: Charles Griffin and Co., Ltd. 1913.

THE third edition of this work, which is undoubtedly the most exhaustive in the English language on the subject of petroleum, has been issued in three volumes. The author has had the assistance of many distinguished collaborators, including Mr. W. H. Dalton, Mr. L. V. Dalton, Prof. V. B. Lewes, Major A. Cooper-Key, and others, in revising the text and bringing the bibliography down to date. The division into sections originally adopted is still preserved, and the book gives a comprehensive and detailed account of the sources, nature, uses, properties, and testing of petroleum and allied products, while the legislative enactments relating to the subject are reproduced in full, and with the bibliography occupy a large part of the third volume.

Elementary Agricultural Chemistry. By HERBERT INGLE, B.Sc. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

THIS book will be found a useful introduction to the study of scientific agriculture by those whose knowledge of chemistry is very limited. A short summary is given of the principles of inorganic chemistry, which is as complete and clear as can reasonably be expected in view of the magnitude of the subject and the very limited amount of space which can be devoted to it. The author has had a specially wide experience of agricultural work in South Africa, and pays a good deal of attention to the problems and conditions met with there and in sub-tropical and tropical regions generally, so that Colonial readers and future colonists may find the book better suited to their needs than a text-book based upon English or European practice only. The second edition has been thoroughly revised, and a few errors and omissions have been rectified.

Industrial Poisoning. By Dr. J. RAMBOUSEK. Translated and Edited by THOMAS M. LEGGE, M.D., D.P.H. London: Edward Arnold. 1913.

MUCH work on industrial poisoning has been done on the Continent, and the author of this book has a very extensive knowledge of the subject, which he has now placed at the disposal of the public. The scope of the book is wide, and in the words of the prelace it is "intended for all who are, or are obliged to be, or ought to be interested in industrial poisoning." Short accounts are given of various processes which are known to have injurious effects upon the health of the workers engaged in them. Some important recent cases are discussed, with full particulars, but the text is not overloaded with historical facts. The symptoms of poisoning by different agents are described, and preventive measures are very comprehensively treated, while social and legislative precautions taken in Germany and elsewhere are given full consideration. The translating and editing has been efficiently performed, and the translator has added some useful notes.

CORRESPONDENCE.

SOME CURIOUS ATOMIC WEIGHT RELATIONS.

To the Editor of the Chemical News.

SIR,—Several years ago I pointed out some curious relations between the atomic weights of argon, iron, bromine, and silver (CHEMICAL NEWS, c., 37) It may be of some interest to note that the same characteristic relations may be extended to a similar series of elements, which leads one to the supposition that an inactive gas, of atomic weight 9·75, exists.

The following table shows such an extension :—

At. wts.	Differences.	At. wts.	Differences.
[Ar = 39·9]			
	—— 0		
	——16 (*c*)		
Ar = 39·9		(?) = 9·75	
	——16		——49·25
	—— 8 (*b*)		——18 6 (b_1)
Fe = 55·9		Co = 59·00	
	——24		——67·92
	—— 4 (*a*)		—— 9·3 (a_1)
Br = 79·9		I = 126·92	
	——28		——77·25
Ag = 107·9		Tl = 204·17	

$2a = b$; $2b = c$. $2a_1 = b_1$.

$a + b + c = 28$. $a_1 + b_1 = 28$.

Notes.—The intervening active elements between argon and iron = 6 or 7; between iron and bromine = 8; between bromine and silver = 9. Similarly, the elements between "9·75" and cobalt = 20 or 21; between cobalt and iodine = 22 or 23; between iodine and thallium = 24 or 25. Uncertainty exists as regards the exact number of intervening elements, or the numerical or chemical order that should be observed in counting some of them. The value "9·75" was arrived at by a curve method described in the citation above. The continuation of the right hand series would lead to an argon analogue of atomic weight about 21·7. The above atomic weight values of the known elements are in practical agreement with the present experimental values. Not knowing the exact values of the decimal fractions of a_1 and b_1, the idea of the greatest possible symmetry in these values, relative to the whole numbers, is shown by giving them the repeating characteristics indicated, which is obviously in accordance with the scheme of geometrical progression involved.

The significance of these relations rests partly upon the close similarity of the parallel elements. The nearest related element to iron is undoubtedly cobalt. Similarly,

bromine has its nearest higher analogue in iodine. Silver is more difficult to match in the same way, but from the following considerations thallium is perhaps eligible for the place. I will quote respectively from (1) Bloxam's "Chemistry," 1895, p. 432; (2) Senter's "Inorganic Chemistry," 1911, pp. 472—473; (3) Mellor's "Modern Inorganic Chemistry," 1912, p. 637:—(1) . . . "But thallium appears to be more nearly related to another monatomic metal, silver, by the sparing solubility of its chloride and the insolubility of its sulphide." (2) "The thallous salts resemble those of the alkalis, inasmuch as the hydroxide and carbonate are soluble in water, whilst the relatively slight solubility of the thallous halides recalls the silver halides. In its trivalent compounds thallium resembles aluminium and gold . . . thallic iodide, TlI_3 . . . is isomorphous with the tri-iodides of rubidium and cæsium." (3) "The physical properties of the metal (thallium) closely resemble lead, and its compounds are related to aluminium, gallium, and indium, much as gold is related to the alkali metals, and mercury to zinc and cadmium. Thallium forms a series of thallous salts similar in properties to mercurous and silver salts. The thallic salts are not very stable, and they behave somewhat like the auric salts."

Mention should be made of the work of Tutton (*Proc. Roy. Soc.*, Nov. 25, 1909, abstracted in CHEMICAL NEWS, c., 298) "On the Relation of Thallium to the Alkali Metals."

From the above it will be seen that the introduction of thallium in the special series here shown is not purely an arbitrary procedure.

There is probably no final and absolute system of classification that is satisfactory from all points of view, therefore different special groupings should be studied, as they may lead to a better understanding of elemental relations.

A letter of mine in the CHEMICAL NEWS (cvii., 311), and the papers referred to therein, have a bearing on the inactive elements of low atomic weight indicated by the above scheme.—I am, &c.,

—— F. H. LORING.

(P.S.—The alkali metals stand next to the inactive gases, and, if thallium is alled to the former, its neighbouring element, mercury, should have some properties in common with the latter. This is the case in so far as Thomson's "positive ray" experiments bring mercury into line with the argon gases. Mercury is comparatively inert when its liquid state is taken into account, as soft metals are usually very active chemically).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 22, June 2, 1913.

1-Benzoyl-2-Phenyl-Δ_1-Cyclopentene. — Edouard Bauer.—When sodamide acts upon 1-benzoyl-2 phenyl-Δ_1-cyclopentene the reaction is the same as with benzophenone. Two sets of crystals are obtained, one melting at 135° and the other at 23°. The former are the amide of 2-phenyl-Δ_1-cyclopentene-1-carbonic acid, the other product being benzene, while the crystals melting at 23° are 1-phenyl-Δ_1-cyclopentene.

Researches on Carpiline.—E. Léger and Ferdinand Roques.—When carpiline is heated to 140° with water in sealed tubes for ten hours two new bases are obtained, one soluble and the other insoluble in cold water. The former is Pyman's pilosinine, and the latter anhydropilosinine. Pyman supposes that carpiline has a constitution like that of pilocarpine, the group C_6H_5—CHOH— replacing the C_2H_5 group of pilocarpine. Probably it contains the group C_6H_5—CHOH – CH, which, under the influence of heat, splits into C_6H_5 – COH and CH_2. At the same time by the loss of water it gives the group C_6H_5—CH = C, which is present in anhydropilosine.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 8, 1913.

Activation of Chlorate Solutions by Osmium.—K. A. Hofmann, O. Ehrhart, and Otto Schneider.—Traces of osmium tetroxide convert neutral chlorate solutions into strong oxidising agents, and the authors' experiments show that this action is due to the addition of chlorate to the osmium tetroxide and the formation of a substance of high oxidation power.

Preparation of Molybdenum and Tungsten Carbides.—Siegfried Hilpert and M. Ornstein.—Molybdenum and tungsten carbides can be obtained by treating the powdered metals with methane or carbon monoxide at high temperatures. The limits of the absorption of carbon correspond to simple stochiometric proportions. In the case of molybdenum the limiting values correspond to Mo_2C for 600° and 1000°. At 800° the composition varies between MoC and Mo_2C_3. Tungsten is converted into W_3C_4 by carbon monoxide at 1000°, and at 800° by methane-hydrogen (1:1) into the carbide, WC. The carbides are also obtained if the trioxides are used instead of the metals.

Mutual Expulsion of Metals from their Phenyl Compounds.—Siegfried Hilpert and Gerhard Grüttner.—By simple replacement of mercury in organic compounds alkyl derivatives of beryllium, magnesium, aluminium, zinc, and phenyl derivatives of magnesium and aluminium can be obtained. Cadmium exhibits only a very slight tendency to form organic compounds, although the authors have obtained cadmium diphenyl $Cd(C_6H_5)_2$. Magnesium halogen alkyls can be used to prepare compounds of less electropositive metals, such as tin, lead, and mercury. The sensitiveness of phenyl compounds towards air and water increases with increasing atomic weight and increasing electronegative character of the metal in question.

Arsenious Compounds.—A. Michaelis and Arthur Schäfer.—The compounds of arsenic often possess a higher molecular weight than the corresponding nitrogen compounds. In order to see whether this held good for arseno-benzene and arseno-toluene the authors determined their molecular weights (the former by the rise of the boiling-point of a benzene solution, and the latter by the lowering of the freezing-point of a phenol solution). The formulæ were thus found to be $C_6H_5.As{:}As.C_6H_5$ and $C_7H_7.As{:}As.C_7H_7$ respectively, and the arsenious compounds are the true analogues of the azo-compounds.

Determination of Nitric Oxide and Oxygen Gasometrically.—Gabriel Klinger.—Nitrogen trioxide is formed when nitric oxide comes into contact with oxygen or air, and in presence of caustic potash potassium nitrite is formed. Oxygen can be determined by means of nitric oxide, or the latter by means of oxygen by passing the one gas into a pipette containing *dry* potash, then introducing the other gas, and after a few seconds determining the absorption by the KOH. The equation is $4NO + O_2 = 2N_2O_3$, and thus four-fifths of the contraction represents the NO and one fifth the oxygen.

Calcium Boride.—E. Wedekind.—Calcium boride can be prepared by heating a mixture of finely-powdered calcium borate and metallic calcium (3 : 5) in a vacuum. The boride thus obtained is a crystalline light brown powder of sp. gr. 2·11. It conducts electricity, and electrodes made of it undergo partial oxidation, giving a mass which is as hard as diamond. It is partially oxidised when heated in air. It is stable towards acids (with the exception of nitric acid), and also towards liquid alkalis, but is decomposed when fused with potash or soda.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2805.

THE INFLUENCE OF CHLORINE ON THE DETERMINATION OF NITRATES BY THE PHENOL DISULPHONIC ACID METHOD.

By ROBERT STEWART and J. E. GREAVES.

The question involved in this study is of fundamental importance in the determination of nitrates in cultivated soils of the arid west, which may be impregnated with alkali. Earlier work at this laboratory on this question demonstrated a marked influence of chlorine upon the amount of nitrates found (Stewart and Greaves, *Journ. Am. Chem. Soc.*, 1910, xxxii., 756). Thus, it was found that if the soil solution contained even as low a concentration as 2·6 parts per million of chlorine in the soil extract less nitrates were found by this method than were actually present.

The experimental data recently presented by Lipman and Sharp (*Univ. of Cal. Publication in Agr. Sci.*, 1912, i., 12), although they are apparently not aware of this fact, confirm this conclusion. This may be seen by converting the results obtained in both cases to the same basis in order to make a comparison, since our results are reported as parts per million of chlorine in the *soil extract*, while Lipman and Sharp's results are reported as milligrms. of sodium chloride present.

The results converted to the same basis, *i.e.*, milligrms. of sodium chloride actually present in the portion of the solution used, are compared in Table I.

Table I.—*Influence of Ionic Chlorine on the Determination of Nitrates in Solution.*

By Stewart and Greaves.

Mgrm. NaCl.	Nitric nitrogen added.	Nitric nitrogen found.	Nitric nitrogen found (per cent).
0·04	0·01	0·01	100
0·09	0·01	0·01	100
0·13	0·01	0·01	100
0·27	0·01	0·009	90
0·52	0·01	0·0094	94
0·79	0·01	0·0086	86

By Lipman and Sharp.

NaCl.	Nitric nitrogen added.	Nitric nitrogen found.	Nitrogen found (per cent).
0·01	0·05	0·051	102
0·05	0·05	0·051	102
0·10	0·05	0·049	98
0·25	0·05	0·045	90
0·50	0 05	0·041	82
1·00	0·05	0·035	70

Thus, it may be readily seen that when only 0·1 mgrm. of sodium chloride was present in both cases all of the nitrates present could be easily determined. Lipman and Sharp, however, found that when 0·25 mgrm. of sodium chloride was present, that only 90 per cent of the nitrates actually present could be determined, while we found that when 0·27 mgrm. of sodium chloride was present, only 90 per cent of the nitrates could be found. With a concentration of 1 mgrm., Lipman and Sharp found only 70 per cent of the nitrate, while we, with 0·79 mgrm. of sodium chloride, found only 86 per cent of the nitrate. It is thus seen that Lipman and Sharp have confirmed, in a remarkable manner, the results obtained at this laboratory. It is seldom that investigators in separate laboratories get such concordant results. It is thus fully confirmed that ionic chlorine has a marked influence on the determination of nitrates in the soil extract, and that in alkali soils this fact must be taken into consideration in determining the nitrate content.

There is still another phase of this question, however, one which, so far as we are aware, has never been considered by previous investigators, and this is the influence of chlorine, which is not in the ionic form but is combined in the organic molecule, on the determination of the nitrate content of the soil extract. This is a question of considerable practical importance, since chloroform is frequently used to inhibit the action of bacteria in the soil extract. Especially is this so in case of the use of the lime method as proposed by Lipman and Sharp. In the use of this method, if chloroform be also used, it appeared to us that there is the possibility of the formation of ionic chlorine from the organic chlorine of the chloroform, and if present in sufficient quantities this would materially affect the value of the results obtained. The assumption that ionic chlorine would be formed by the action of calcium oxide on the chloroform seemed to be justified by the fact that is so well known, that potassium hydroxide does act on chloroform as indicated in the following equation: $CHCl_3 + KOH = HCOOK + 3KCl + 2H_2O$, with the production of ionic chlorine. This being the case why may not calcium hydroxide act in a similar manner, as follows: $2CHCl_3 + 4Ca(OH)_2 = (HCOO)_2Ca + 3CaCl_2 + 4H_2O$?

If such a reaction did take place, the ionic chlorine formed would materially interfere with the determination of the nitrates. In view of the fact that we are aware that chloroform is used by some investigators with the lime method, it appeared to us that the question should be exhaustively studied.

Therefore, varying amounts of chloroform were added to solutions containing 1 mgrm. of nitric nitrogen and 1 grm. of lime. These solutions were carefully worked up in a mortar, placed in a closed container, and allowed to stand over night. A portion of the solution was used the next morning to determine the ionic chlorine present, while in another portion the nitric nitrogen was determined. The results obtained are given in Table II.

An examination of the data presented in Table II. brings out two very important facts. First, that ionic chlorine is liberated when lime and chloroform are mixed together, and that the quantity of chlorine liberated varies with the chloroform. Second, that the ionic chlorine formed interferes very greatly with the accurate determination of nitrates by the phenol disulphonic acid method. It may, therefore, be seen that determinations made by this method, where the solution has both chloroform and lime present, give results which may be less than one-half of what they should be.

Table II.—*Influence of Chloroform on Determination of the Nitric Nitrogen by the Lime Method.*

Sample No.	Lime added.	Chloroform added. Cc.	Nitric nitrogen added. Mgrm.	Nitric nitrogen found. Mgrm.	Per cent loss.	Ionic chlorine found, mgrms. sodium chloride.
1.	1·0	none	1·0	1·0	none	none
2.	1·0	0·1	1·0	0·54	46	2·0
3.	1·0	0·2	1·0	0·37	63	5·2
4.	1·0	0·3	1·0	0·47	53	8·6
5.	1·0	0·4	1·0	0·24	76	11·4
6.	1·0	0·5	1·0	0·23	77	12·8
7.	1·0	0·6	1·0	0·37	63	16·3
8.	1·0	0·7	1·0	0·44	56	26·3
9.	1·0	0·8	1·0	0·32	68	32·0
10.	1·0	0·9	1·0	0·40	60	37·9
11.	1·0	1·0	1·0	0·40	60	41·3

As a further check on the influence of chloroform on the determination of nitric nitrogen, a great number of determinations were made on solutions containing varying amounts of nitric nitrogen, both with and without the

addition of chloroform. In the case where chloroform was added, a few drops were shaken into the solution, just as is the case where it is added to prevent bacterial action while the solution is standing. The results are given in Table III.

TABLE III. — *Determination by Lime Method of Nitric Nitrogen Present in Solution to which Known Amounts of Nitrate was Added.*

Sample No.	Nitric nitrogen added.	Nitric nitrogen found (mgrms.). 1st trial.	2nd trial.	3rd trial.	4th trial.	Average.
		Without Chloroform.				
1.	none	none	none	none	none	none
2.	1·0	0·88	0·90	1·0	0·82	0·90
3.	1·5	1·5	1·50	1·53	1·43	1·49
4.	2·0	2·0	2·0	2·05	2·00	2·01
5.	3·0	3·0	3·05	3·2	3·15	3·10
		With Chloroform.				
1.	none	none	none	none	none	none
2.	1·0	0·29	0·32	0·40	0·55	0·39
3.	1·5	0·52	0·70	0·63	0·78	0·66
4.	2·0	0·84	1·10	0·92	1·08	0·99
5.	3·0	0·69	1·20	1·15	1·52	1·14

These results show conclusively that in the absence of chloroform concordant results were obtained by this method, and that practically all of the added nitrate could be accurately recovered. When, however, chloroform was added to the solution containing the nitrate and calcium hydroxide, it was impossible to obtain concordant results, and the amount of nitric nitrogen found had no apparent relationship to the amount of nitric nitrogen actually present. It may thus be seen that the chloroform in the presence of calcium hydroxide very materially interferes with the accurate determination of the nitric nitrogen.

The discussion so far has had to do only with the determination of the nitrates in solution. The soil factor must be considered. Accordingly, it was decided to determine the nitric nitrogen content in two soils, one a very rich hothouse soil, the other a field soil, poor in nitric nitrogen. The nitric nitrogen was determined by the lime method both with and without chloroform. The results obtained are recorded in Table IV.

TABLE IV.—*Comparative Determination of Nitric Nitrogen in a Soil.*

Sample No.		Soil rich in nitrates.	Soil poor in nitrates.
	Without Chloroform.		
1.	Lime 1 grm. per 50 grms. of soil	27·0	0·36
	Lime 1 grm. per 50 grms. of soil	27·5	0·36
	With Chloroform.		
7.	Lime and chloroform	22·5	0·22
8.	Lime and chloroform	22·0	0·14

Again the marked influence of chlorine is demonstrated. In the rich soil where chloroform and lime are used there is a loss of 5 mgrms. of nitric nitrogen, while in the soil poor in nitric nitrogen there is a loss of over 50 per cent of the nitrates, and, furthermore, the results obtained are not concordant.

It is seen, therefore, that the lime method is highly desirable for use in soils rich in nitrates and organic matter, since a clear solution is thus obtained and there is no interference in the determination of the nitrates, provided chloroform is not also used.

Ionic chlorine has a marked influence on the determination of the nitrates in the solution whether the ionic chlorine is derived from the chlorides of the soil or by decomposition of the added chloroform. The result obtained also indicated clearly that chloroform should not be added to the soil extract obtained by the lime method.—*Journal of the American Chemical Society*, xxxv., No. 5.

ON THE NITRILE OF FUMARIC ACID AND THE PREPARATION OF METHYL MALEATE.

By EDWARD H. KEISER and L. McMASTER.

In the synthesis of fumaric and maleic acids from acetylene by means of the iodides and potassium cyanide the nitriles of the acids were not isolated. Subsequently E. H. Keiser and J. J. Kessler (*Am. Chem. Journ.*, xlvi., 523) obtained the nitrile of fumaric acid by heating fumaramide with phosphorus pentoxide. The long slender needles that formed as a sublimate undoubtedly had the composition of fumaric nitrile. They had a pleasant odour, and when treated with alkalis gave off ammonia. In short, the behaviour of the substance was such as one would expect from a cyanide. Difficulty was experienced, however, in trying to convert the fumaric nitrile into fumaric acid. This was no doubt due to the fact that the quantities worked with were small. We have now prepared the nitrile in larger quantities, and have succeeded in converting it back into fumaramide and into fumaric acid, thus establishing, beyond all doubt, its constitution.

This conversion was found to take place readily by means of an alkaline solution of hydrogen dioxide (*Ber.*, xviii,, 355), the action taking place according to the equation :—

$$\begin{matrix} CHCN \\ \| \\ CHCN \end{matrix} + 2H_2O_2 = \begin{matrix} CHCONH_2 \\ \| \\ CHCONH_2 \end{matrix} + O_2.$$

The fumaramide thus formed was then transformed into fumaric acid by warming with dilute caustic potash.

Twenty-five hundredths grm. of fumaric nitrile was treated with 25 cc. of a 3 per cent solution of hydrogen dioxide, and the liquid made faintly alkaline with a few drops of caustic soda solution. There was a rapid evolution of oxygen, and after a short time a white precipitate separated. This was removed by filtration, and was found to be insoluble in cold water, in alcohol, and ether, but was soluble in hot water, thus showing the properties of fumaramide. In determining the melting-point, it became black at 232°, and melted completely at 267°. For the sake of comparison a sample of fumaramide was prepared from diethyl fumarate by the action of ammonia, and this behaved in the same way as that obtained from the nitrile. The melting-point of fumaramide is given by Curtius and Koch at 232° "with carbonisation" (*Journ. Prakt. Chem.*, xxxviii., [2], 478). Hell and Poliakow give it at about 266° (*Ber.*, xxv., 643). With a second specimen of the fumaramide made from the nitrile we found that at 233° the substance became black, and at 267° it melted sharply.

The fumaramide thus made from fumaric nitrile was then hydrolysed by warming upon the water-bath for one hour with dilute caustic potash. All odour of ammonia was then gone, and the solution was allowed to cool, and was then neutralised with dilute nitric acid. Silver nitrate was added, and a white precipitate of silver fumarate was formed. This was filtered, washed, and dissolved in dilute ammonia, and re-precipitated by again neutralising with nitric acid. The precipitate, after filtering and washing, was dried at 100°. On analysis the following result was obtained :—

0·0628 grm. substance gave 0·0543 grm. AgCl.

Ag calculated for $C_5H_2O_4Ag_2$ ..	65·4
Ag found	65·1

The dried salt deflagrated like gunpowder when heated, this being one of the characteristic properties of silver fumarate. It was also insoluble in boiling water, a fact which distinguishes it from silver maleate.

Another portion of fumaramide made from the fumaric nitrile by means of hydrogen dioxide was saponified by alcoholic potash. As the amide is only slightly soluble in absolute alcohol, the solution was boiled for sixteen hours. It was then filtered and evaporated to remove the alcohol, water added, and the alkali neutralised with nitric acid.

The silver salt was then precipitated, washed, dried, and analysed.

0·1016 grm. substance gave 0·0877 grm. AgCl.

Ag calculated for $C_4H_2O_4Ag_2$ ..	65·4
Ag found	65·0

Dimethyl Maleate.—This ester has heretofore been made by the action of methyl iodide upon silver maleate. We have succeeded in preparing it from methyl alcohol, maleic acid, and sulphuric acid. Five grms. of maleic acid, 50 cc. of methyl alcohol, and 2 cc. of concentrated sulphuric acid were boiled for four hours under an inverted condenser. The liquid was then poured into an evaporating dish, and the alcohol allowed to evaporate. The residue was stirred up with barium carbonate, and allowed to stand in contact with it for several days. Ether was added to the mixture, and the solid matter separated by filtration. The ether was removed from the filtrate by evaporation, and the thick oily residue, consisting of dimethyl maleate, was distilled. Its boiling point was found to be 203°. A small quantity of a solid melting at 102° was found in the condenser; this was dimethyl fumarate. That the clear distillate was dimethyl maleate was proved by adding bromine water to a portion of it. On standing a white solid crystalline compound was obtained. This was re-crystallised from its solution in ether. It melted at 102°, and had all of the properties of dimethyl fumarate.

We have also studied the action of ammonia upon dimethyl maleate. When a mixture of the ester and ammonia solution was allowed to stand several days, the oil gradually dissolved, but no precipitate of amide was formed as in the case of the dimethyl fumarate. On evaporating slowly, after the ammonia and water were removed, thick yellowish oil remained, which became semi-solid when it was stirred, and was very difficult to detach from the platinum dish in which it was contained. A portion of it, when heated, acquired a red colour. Another portion, when mixed with phosphorus pentoxide, gradually became hot, and as the mass turned black a white sublimate came off which was condensed in an inverted funnel. This sublimate melted at from 135° to 138°, and may have been the nitrile of maleic acid. A third portion was warmed with caustic soda, and ammonia was given off. In all probability this thick glue-like mass was the amide of maleic acid.—*American Chemical Journal*, xlix., No. 2.

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS.*

By YOSHITO YAMAUCHI.

(Concluded from p. 92).

II. *Reactions of Ozone Investigated according to this Method* (continued).

4. *Thallous Nitrate.*—Schönbein first studied the oxidation of thallium or thallous hydroxide by ozone in the presence of water (*Journ. Prakt. Chem.*, 1864, xciii., 36; 1865, xcv., 470). Schöne applied this reaction to the quantitative analysis of ozone (*Ber.*, 1880, xiii., 1508), making use of test-paper soaked in thallous hydroxide solution, where the depth of the colour of the thallic oxide formed should vary according to the amount of ozone present. Lamy settled the composition of thallic oxide, dried at 100°, to be $Tl_2O_3.H_2O$ (*Ann. Chim. Phys.*, lxvii., [3], 385), while Rabe claims to have obtained the anhydrous oxide Tl_2O_3 by oxidising an alkaline solution of a thallous salt with hydrogen peroxide (*Zeit. Anorg. Chem.*, 1906, xlviii., 428).

According to the author's experiments, the water in the thallic oxide seems never to be equal to one molecule, as was shown by Lamy. So it may be urged that hydrated thallic oxide is very liable to lose its water in part even when dried below 100°. He also determined as usual the amount of thallic oxide precipitated equivalent to the ozone used, from the results of which the equation for the reactions could be well established.

An ammoniacal solution of thallous nitrate was taken for the purpose of experiment. An aliquot portion, after being introduced into the tube containing ozone, was shaken vigorously for a few minutes only. The voluminous brown precipitate was then washed, collected on a weighed filter, dried in an air-bath below 100°, and finally weighed. The results of the experiment are given in Table VII.

TABLE VII.

No.	Ozone, in grm.	Thallic oxide precipitated by the action of ozone, in grm.	Thallic oxide per grm. ozone, in grms.
1 ..	0·0206	0·1038	5·04
2 ..	0·0151	0·0618	4·09
3 ..	0·0201	0·0952	4·74
4 ..	0·0147	0·0750	5·10
5 ..	0·0139	0·0716	5·15
6 ..	0·0182	0·0857	4·71
7 ..	0·0139	0·0635	4·57
Mean			1 : 4·77

If the reaction be represented as follows:—

$$2TlOH + 2O_3 = Tl_2O_3 + H_2O + 2O_2 \quad . \; . \; 10,$$

and the oxide be considered to retain no water at all, then the ratio of ozone to the oxide formed is 1 : 4·76, in good accord with the experimental data.

Now, in the hope that the composition of thallic oxide might be better established, the author converted 0·5096 grm. of well dried oxide into thallic chloride, added a certain quantity of potassium iodide, and then determined the amount of iodine liberated from it. The amount of thallium equivalent to iodine was calculated from the equation—

$$TlCl_3 + 3KI = TlI + 3KCl + I_2 \quad . \; . \; . \; 11,$$

and then re-calculated to thallic oxide, Tl_2O_3, with no water, as 0·4970 grm. The loss of weight from the original 0·5096 grm., about 2·4 per cent, may be due to some quantity of water still retained.

That the oxidation of a thallous salt by ozone goes on rapidly and completely, and that the thallic oxide thus formed can be very easily weighed, affords surely another very convenient method for the gravimetric determination of ozone in contrast to that of Schöne (*loc. cit.*). It is then only necessary to take proper care to dry the oxide always at a constant temperature, in order to have the water regularly expelled.

5. *Mercurous Nitrate.*—According to Mailfert (*Comptes Rendus*, 1882, xciv., 860), mercurous salts in solution are easily oxidised by ozone partly to mercuric salts, which go into solution, and partly to basic salts, which remain undissolved.

The author examined the action of ozone on mercurous nitrate in the presence of an excess of nitric acid, and found that the oxidation takes place, though very slowly and incompletely, there remaining always some odour of ozone. The formation of basic salts was not perceived, because there was present much excess of nitric acid.

The amount of the mercuric salt formed was determined from the quantity of the unchanged mercurous salt remaining, which was precipitated and weighed in the form of chloride. The results of the experiments are given in Table VIII.

TABLE VIII.

No.	Ozone, in grm.	Mercurous nitrate oxidised by ozone, in grm.	Mercurous nitrate per grm ozone, in grms.
1 ..	0·0100	0·0919	9·19
2 ..	0·0066	0·0614	9·30
3 ..	0·0108	0·1090	10·09
4 ..	0·0110	0·1101	10·01
5 ..	0·0090	0·0807	9·63
Mean			1 : 9·64

* *American Chemical Journal*, xlix., No. 1.

Calculated for the equation—

$$Hg_2(NO_3)_2 + O_3 = HgO + Hg(NO_3)_2 + O_2 \quad . \quad . \quad 12,$$

the ratio of ozone to mercurous nitrate is 1 : 10·94, wherein the difference from the experimental data shows the incompleteness of the reaction.

6. *Ferrous Ammonium Sulphate* (Schönbein, *Liebig's Ann. Chem.*, 1854, lxxxix., 293, makes the statement that the ferrous salt is oxidised by ozone to the ferric state).—A solution of this salt was treated in the usual manner with ozone, and the amount of oxidised salt was determined by subtracting the unchanged ferrous salt, as determined with potassium permanganate, from the total quantity of ferrous salt originally taken. The ratio of the ozone to the oxidised salt was found from the following data :—

TABLE IX.

No.	Ozone, in grm.	Ferrous ammonium sulphate oxidised by ozone, in grm.	Ferrous ammonium sulphate per grm. ozone, in grms.
1 ..	0·0023	0·0332	14·43
2 ..	0·0111	0·1484	13·37
3 ..	0·0047	0·0666	14·17
4 ..	0·0064	0·0809	12·64
		Mean	1 : 13·65

Calculated for the equation,—

$$2Fe(NH_4)_2(SO_4)_2 + O_3 = Fe_2O(SO_4)_2 + 2(NH_4)_2SO_4 + O_2 \quad . \quad . \quad . \quad 13,$$

the ratio is 1 : 11·83. The difference between the experimental ratio and the theoretical must be due to the simultaneous action of ordinary oxygen, as we have seen in the case of stannous chloride.

7. *Tellurous Oxide* (*cf.* Mailfert, *Comptes Rendus*, 1882, xciv., 1186).—By passing ozone into tellurous oxide suspended in water, no appreciable amount of oxidation products could be detected.

8. *Titanium Dioxide.*—Since titanium dioxide dissolved in concentrated sulphuric acid is very easily oxidised by hydrogen peroxide, the author made certain tests as to whether it is also oxidised by ozone. The results, however, were always negative.

9. *Chloropalladious Acid.*—According to L. Wöhler and King (*Zeit. Anorg. Chem.*, 1905, xlvi., 327), oxidation of this compound by ozone takes place in the following manner :—

$$H_2PdCl_4 + 4H_2O + O_3 = Pd(OH)_4 + 4HCl + H_2O + O_2 \quad 14.$$

But, as there was found no convenient way of distinction between the palladic and palladious compounds, the author could not apply his method to test the correctness of the above equation.

Summary.

1, As the concentration of ozone differs with every preparation, all methods of determining the concentration through the consumption of the gas must involve using up the preparation ; *i.e.*, when the concentration is known, the preparation no longer exists. The method of its determination by direct weighing is also not convenient. The author has therefore contrived a new method of dividing one sample into two parts, and of determining the concentration of the one by measuring that of the other by analysis.

2. So far as the author could determine, ozone seems to be decomposed according to the equation $O_3 = 3O$ only in the case of the oxidation of stannous chloride. The decomposition goes on, however, usually as follows :— $O_3 = O_2 + O$.

3. The action of ozone on sodium thiosulphate has been studied by the author perhaps for the first time. There take place two reactions, in which the ozone seems first to cause the catalytic decomposition of the thiosulphate, and then to be able to effect a partial oxidation of the sulphite formed.

4. Formation of thallic oxide from a thallous salt by ozone occurs very rapidly and completely. It may surely be utilised as a gravimetric method in the quantitative determination of ozone.

THE

VOLUMETRIC DETERMINATION OF GOLD.

By VICTOR LENHER.

IT has been shown that sulphurous acid is capable of reducing auric chloride to aurous in the presence of certain other salts (*Journ. Am. Chem. Soc.*, 1913, xxxv., 546). Through the agency of this reagent it is possible to estimate gold volumetrically easily and accurately.

In the following work a sulphurous acid solution was prepared by evolving sulphur dioxide from sodium acid sulphite by means of hydrochloric acid, and, after washing the gas, conducting it into repeatedly distilled water. The strength of the sulphurous acid necessarily varied from time to time, due to its gradual oxidation. Its strength varied from 0·005 grm. Au to 0·002 grm. Au per cc. Sulphurous acid solution requires frequent standardisation, owing to its ability to slowly oxidise by absorbing oxygen from the air in the container and pass over into sulphuric acid. After a large amount of experimentation under widely differing conditions the idea of using a permanganate solution as a convenient standardising solution was abandoned. Working under the most favourable conditions, it has not been found possible to obtain results having an error lower than 1 per cent between permanganate and sulphurous acid.

The most reliable method of standardising sulphurous acid is through the agency of iodine. It is entirely immaterial for the methods to be described whether the sulphurous acid solution is standardised on a known weight of iodine in potassium iodide, or whether solid potassium iodide is dissolved in water acidulated with sulphuric or hydrochloric acid and a definite amount of standard permanganate introduced. As a precaution both of the methods indicated were used continuously, and in addition a gold solution whose content had been determined gravimetrically was also used as a standardisation check on the sulphurous acid solution.

1. Auric chloride when treated with potassium iodide liberates iodine according to the equation—

$$AuCl_3 + 2KI = AuCl + 2KCl + I_2.$$

The iodine thus liberated can be titrated in presence of excess of potassium iodide by means of standard sulphurous acid. Starch can be used as the indicator.

2. Auric chloride can be treated with excess of a strong solution of magnesium chloride, then with potassium iodide, and the liberated iodine titrated with sulphurous acid.

3. Auric chloride when treated with potassium bromide yields bromine thus :— $AuCl_3 + 2KBr = AuCl + 2KCl + Br_2$. The liberated bromine can be titrated with a solution of sulphurous acid.

4. Auric chloride treated with magnesium chloride and potassium bromide similarly liberates bromine, which can be titrated with sulphurous acid.

5. Auric chloride when treated with magnesium chloride gives a yellow colour, which can be decolorised by titration with sulphurous acid.

6. Auric chloride and sodium chloride give a yellow colour which by sulphurous acid can be titrated to the colourless or aurous state.

In order to test the efficiency of these principles auric chloride solutions were prepared by solution of weighed amounts of metallic gold in hydrochloric acid and potassium chlorate, and the excess of chlorine removed by the addition of ammonia until the formation of a permanent precipitate, which was then dissolved in hydrochloric acid.

Unless precautions of this character are taken the gold solution will either contain some free chlorine, on the one hand, or some metallic gold will separate on the other, when an attempt to remove the free chlorine by evaporation to dryness, or nearly to dryness, is made. Evaporation of a pure auric chloride solution, even on the water-bath, causes the production of a small amount of aurous chloride, which on subsequent dilution gradually changes to metallic gold and auric chloride. By the treatment of metallic gold with hydrochloric acid and potassium chlorate followed by the ammonia and hydrochloric acid treatment, an auric solution can be satisfactorily obtained.

Series 1.

Definite amounts of gold chloride, prepared in the manner indicated, and acid with hydrochloric acid were treated in a dilution of 100 cc. with about 3 grms. of potassium iodide, and the iodine liberated was titrated with a standard solution of sulphurous acid with the following results:—

No.	Au taken (grm).	Au found (grm.).	Error.
1.	0·0395	0·0395	—
2.	0·0439	0·0438	−0·0001
3.	0·0878	0·0876	−0·0002
4.	0·1098	0·1092	−0·0006
5.	0·1107	0·1108	+0·0001
6.	0·2289	0·2289	—
7.	0·4395	0·4397	+0·0002
8.	0·7301	0·7302	+0·0001

Series 2.

Gold chloride solutions were treated with an excess of a saturated solution of magnesium chloride, potassium iodide was added, and the titration by means of sulphurous acid effected in a dilution of 100 cc.

No.	Au taken (grm.).	Au found (grm.).	Error.
9.	0·0439	0·0440	+0·0001
10.	0·0878	0·0879	+0·0001
11.	0·1061	0·1063	+0·0002
12.	0·2653	0·2652	−0·0001
13.	0·5305	0·5298	−0·0007

Series 3.

Known amounts of gold chloride solution were treated with excess of a saturated solution of magnesium chloride. The yellow colour of the auric chloride is considerably deepened by the addition of magnesium chloride. When sulphurous acid is added from the burette, the solution is bleached progressively until colourless. No other indicator is necessary.

No.	Au taken (grm.).	Au found (grm.).	Error.
14.	0·0439	0·0438	−0·0001
15.	0·0439	0·0440	+0 0001
16.	0·2289	0·2289	—
17.	0·2289	0·2289	—

In numbers 14, 15, and 16, 25 cc. portions of auric chloride solution containing a small amount of hydrochloric acid were treated with sufficient excess of concentrated magnesium chloride to bring the volume to 100 cc., and titrated. In No. 17 conditions were the same, except that 20 cc. of concentrated hydrochloric acid were present, showing that a considerable amount of free hydrochloric acid does not materially affect this titration of auric chloride in presence of magnesium chloride.

Series 4.

Fifty cc. of the slightly acid solution of auric chloride were brought to a volume of 100 cc. with a saturated solution of sodium chloride, and titrated to a colourless state by means of sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
18.	0·0439	0·0438	−0·0001
19.	0·2289	0·2289	—

In all of the above titrations a decided excess of alkaline salts was present, and at this point the reaction of sulphurous acid was studied on auric chloride solutions containing free hydrochloric acid, but no salts. In such a gold solution sulphurous acid not only does not show a distinct bleaching effect but metallic gold is thrown out of the solution with ease.

Series 5.

Gold chloride containing a small quantity of hydrochloric acid was brought to a volume of 100 cc., 3 to 5 grms. of potassium bromide were added, and the red colour of the free bromine was titrated to colourless by means of sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
20.	0·0439	0·0439	—
21.	0·0439	0·0440	+0·0001
22.	0·0439	0·0438	−0·0001
23.	0·0878	0·0876	−0·0002
24.	0·2289	0·2289	—

Series 6,

Auric chloride solutions were treated with 3 to 5 grms. of potassium bromide, and made up to 100 cc. with a strong solution of magnesium chloride. The red colour of the free bromine was titrated to colourless by sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
25.	0·0439	0·0440	+0·0001
26.	0·1061	0·1063	+0·0002
27.	0·2653	0·2655	+0 0002

In the application of the above methods, the gold is originally usually in the metallic form. In order to dissolve the metal either chlorine water or hydrochloric acid and potassium chlorate are convenient solvents. The excess of the oxidising agent cannot be removed by evaporation on account of the production of some aurous chloride. The free chlorine can be advantageously removed by addition of ammonia until a permanent precipitate forms, acidulating with hydrochloric acid, and heating to re-dissolve the precipitate formed by the ammonia. On cooling, 3 grms. of potassium iodide are added, and titration is effected by a standard solution of sulphurous acid, using, if desired, starch as the indicator; or, instead of using potassium iodide, the solution can be treated with potassium bromide or with excess of sodium chloride and titrated by sulphurous acid. —*Journal of the American Chemical Society*, xxxv., No. 6.

THE ACTION OF THIONYL CHLORIDE ON THE OXIDES OF METALS AND METALLOIDS.

By H. B. NORTH and A. M. HAGEMAN

THE action of thionyl chloride on oxides of metals and metalloids has been studied but little. The first research of this nature appears to have been made by Lenher and North (*Journ. Am. Chem. Soc.*, 1907, xxix., 33), who investigated the reaction of thionyl chloride on selenium dioxide in 1907. This work was followed in 1908 by a study of the reaction on tellurium dioxide by Lenher and Hill (*Ibid.*, 1908, xxx., 738). In 1910 North (*Ibid.*, 1910, xxxii., 184) investigated the reaction of thionyl chloride on both the red and yellow varieties of mercuric oxide.

In each of the above mentioned investigations reaction was found to proceed readily at elevated temperatures, with the formation of the chloride of the metal and the corresponding production of sulphur dioxide. The reactions were carried out in sealed glass tubes.

In 1911 Darzens and Bourion (*Comptes Rendus*, 1911, cliii., 270) investigated the reaction of thionyl chloride on a number of oxides, chiefly those of rare earths. They found that with ThO_2, La_2O_3, Sm_2O_3, ZrO_2, and Cr_2O_3 the

corresponding chlorides were formed, while V_2O_5 yielded the oxychloride $VOCl_3$, and WO_3 gave a mixture of the two oxychlorides, WO_2Cl_2 and $WOCl_4$. TiO_2 gave a peculiar compound which they supposed to be a sulphochloride, and Gd_2O_3 gave a mixture of chloride and oxychloride.

It is very probable that Darzens and Bourion made no examination of the by-products formed, inasmuch as no mention was made of them and equations were not given for the reactions.

In general, the action of thionyl chloride on an oxide of a metal results in the formation of a chloride of the metal and the liberation of sulphur dioxide. This reaction can be represented by the following general equation in which "M" represents a divalent metal:—

$$MO + SOCl_2 = MCl_2 + SO_2.$$

There are cases, however, for which this type equation does not hold. For example, with a metal having two series of salts, the lower oxide, when treated with a decided excess of the reagent, gives rise to the higher chloride; hence the reagent appears to act first as a chlorinating agent and then as an oxidising agent. If "M" in the above equation represents a metal which is tetravalent as well as divalent, the reaction first proceeds as above with the formation of the dichloride; and this compound is then oxidised to the tetrachloride according to the equation—

$$3MCl_2 + 4SOCl_2 = 3MCl_4 + 2SO_2 + S_2Cl_2.$$

By combining the two equations we obtain the following:—

$$3MO + 7SOCl_2 = 3MCl_4 + 5SO_2 + S_2Cl_2.$$

In such an oxidising reaction, the by products are always sulphur dioxide and sulphur monochloride.

All of the reactions to be described in this paper were carried out in sealed glass tubes, and with one or two exceptions a temperature of 150—200° was employed. In each experiment about 1 grm. of the oxide, carefully dried, was treated with an excess of the reagent. All of the oxides were as pure as could be obtained.

Zinc Oxide.—Zinc oxide and thionyl chloride were heated together in sealed glass tubes for several hours at 150° without any apparent change in appearance. However, when the tubes were opened considerable pressure due to sulphur dioxide was noted. The white powder was well washed with carbon disulphide, dried, and weighed. It was then dissolved in water containing a few drops of nitric acid. Determination of chlorine and zinc proved the compound to be anhydrous zinc chloride, $ZnCl_2$; hence the reaction undoubtedly proceeded according to the equation $ZnO + SOCl_2 = ZnCl_2 + SO_2$. Judging from the fine state of division, it is probable that anhydrous zinc chloride is only slightly soluble in thionyl chloride.

Cadmium Oxide.—Thionyl chloride was found to have no action on cadmium chloride in the cold, but when heated at 200° in sealed glass tubes the brown colour of the oxide gradually disappeared with the simultaneous production of a white non-crystalline compound. This proved upon analysis to be cadmium chloride, $CdCl_2$; hence the reaction proceeds according to the equation $CdO + SOCl_2 = CdCl_2 + SO_2$. It is evident that cadmium chloride, like zinc chloride, is at best only slightly soluble in thionyl chloride and liquid sulphur dioxide.

Arsenic Trioxide.—In the case of arsenic trioxide the reaction proceeds in the cold and the oxide gradually goes into solution. It was naturally thought that the reaction follows the equation $As_2O_3 + 3SOCl_2 = 2AsCl_3 + 3SO_2$. Inasmuch as arsenic trichloride is a liquid and remains mixed with the excess of thionyl chloride and liquid sulphur dioxide, a quantitative separation is difficult. Furthermore, although arsenic trichloride boils at 130° and thionyl chloride at 78°, separation by fractional distillation is difficult owing to the small quantities of material used. A single fractionation was made, however, the portion boiling below 128° being rejected and that boiling between 128° and 132° being retained. The latter was examined qualitatively, and was found to contain arsenic in the trivalent form in addition to considerable chlorine. From this it was assumed that the above equation is correct, and that arsenic trichloride was formed.

Other experiments were performed in which a decided excess of thionyl chloride was employed at a temperature of 200°, but these, upon examination in the manner described above, gave the same tests; hence they undoubtedly contained the same compound.

Antimony Trioxide.—Antimony trioxide was found to react immediately with thionyl chloride at the ordinary temperature with liberation of considerable heat. The oxide dissolved completely in the reagent, but upon cooling white crystals of antimony trichloride separated. The reaction proceeds according to the equation $Sb_2O_3 + 3SOCl_2 = 2SbCl_3 + 3SO_2$.

Other experiments were made in which a large excess of thionyl chloride was used, and the tubes were sealed and heated at 150° for several hours. Upon cooling, no crystalline deposit was formed; hence it was supposed that the excess of thionyl chloride had oxidised the antimony chloride to pentachloride according to the equation $3SbCl_3 + 4SOCl_2 = 3SbCl_5 + 2SO_2 + S_2Cl_2$; or, representing the entire reaction by a single equation, $3Sb_2O_3 + 17SOCl_2 = 6SbCl_5 + 13SO_2 + 2S_2Cl_2$. The liquid contents of the tubes were examined carefully and were found to contain pentavalent antimony, sulphur dioxide, and sulphur monochloride; hence the authors are confident that the reaction proceeds according to the equations given above. No attempt was made to separate the products quantitatively.

Bismuth Trioxide.—Bismuth trioxide, in contrast to arsenic and antimony trioxides, was unattacked by the reagent at the ordinary temperature, but after heating for several hours at 150—200° the formation of small white crystals was noted. These crystals analysed to $BiCl_3$; hence reaction proceeds according to the equation $Bi_2O_3 + 3SOCl_2 = 2BiCl_3 + 3SO_2$.

Ferric Oxide.—Although ferric oxide is not at all attacked by thionyl chloride at the ordinary temperature, when heated at 150° the reaction proceeds readily with the formation of anhydrous ferric chloride in large green hexagonal plates, which by transmitted light are red in colour. The reaction evidently proceeds as follows:—$Fe_2O_3 + 3SOCl_2 = 2FeCl_3 + 3SO_2$. Judging from the size of the crystals, it is evident that anhydrous ferric chloride is exceedingly soluble in thionyl chloride at elevated temperatures. In all respects the crystals appear to be identical with those obtained by the action of thionyl chloride (North and Hageman, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 890) and sulphuryl chloride (North, *Bull. Soc. Chim.*, 1911, [4], ix., 646) on metallic iron.

Glucinum Oxide.—Glucinum oxide was found to be unattacked by thionyl chloride even after tubes containing the oxide and reagent had been heated at 200° for thirty hours.

Calcium Oxide and Strontium Oxide.—Neither calcium nor strontium oxide were found to be attacked by thionyl chloride at temperatures up to 200°.

Magnesium Oxide.—Magnesium oxide, which had been strongly ignited and cooled over sulphuric acid, was heated with thionyl chloride for twenty-four hours at a temperature of 150—200°. The white powder, which to all appearances had not changed, was well washed with carbon disulphide, dried, and weighed. Analysis showed it to be $MgCl_2$; hence reaction evidently proceeds according to the equation $MgO + SOCl_2 = MgCl_2 + SO_2$.

Two other samples of magnesium oxide, which were tested without previous blasting, were found to react readily at slightly elevated temperatures, due, undoubtedly, to the presence of considerable magnesium hydroxide.

Silver Oxide.—Silver oxide was found to be unattacked by the reagent in the cold, and even after heating for several hours at 150° reaction had apparently not taken place, inasmuch as the brown powder appeared to be unchanged. The tubes were opened, the brown powder was

well washed with carbon disulphide, dried, and examined qualitatively. It was found to contain a trace of silver chloride. It is possible that the reaction proceeded to a slight extent and that the silver chloride formed, due to its insolubility in the reagent, served to protect the remainder of the oxide.

Cupric Oxide.—Cupric oxide was not attacked by the reagent at the ordinary temperature, but after the tubes containing the two were heated at a temperature of 200° for several hours, they were found to contain a brownish green non-crystalline powder. This substance was washed, dried, and analysed, and was found to be anhydrous cupric chloride, $CuCl_2$; hence the reaction took place according to the equation $CuO + SOCl_2 = CuCl_2 + SO_2$.

Cuprous Oxide.—Cuprous oxide, like the higher compound, was found to react with thionyl chloride at about 200°, and the product formed was cupric chloride, $CuCl_2$. Inasmuch as the reaction is one of oxidation as well as chlorination, it was thought that it proceeds according to the equation $Cu_2O + 4SOCl_2 = 2CuCl_2 + S_2Cl_2 + SO_2$. When the tubes were opened they were found to contain sulphur dioxide and sulphur monochloride in addition to the excess of the reagent; hence the equation above is undoubtedly correct.

Aluminium Oxide, Chromic Oxide, and Tin Dioxide.—These compounds were entirely unattacked by thionyl chloride, even after being heated with the reagent at 200° for hours. This is not surprising, however, inasmuch as these compounds are little attacked by reagents in general, especially after having been highly heated.

As mentioned at the beginning of this paper, Darzens and Bourion state that chromic oxide is changed to the chloride by thionyl chloride at elevated temperatures, though they make no mention of the temperature employed. It is possible that the oxide used by Darzens and Bourion may have been made at a correspondingly low temperature, or it may possibly have contained a trace of moisture. The authors of this article have been absolutely unable to bring about even the slightest reaction between chromic oxide and thionyl chloride at temperatures up to 200°.—*Journal of the American Chemical Society*, xxxv., No. 4.

PHOSPHATIC FERTILISERS.*

By Prof. W. PALMAER.

In order to meet the ever growing demand of agriculture for phosphate fertilisers, chiefly the following preparations are at present produced:—Acid phosphate, basic slag, bone meal, bicalcic phosphate, which are here given in the order corresponding to the amount produced, acid phosphate being the phosphate fertiliser most largely produced, the annual output amounting to about 10,000,000 tons.

Bicalcic phosphate so far has been produced only in small quantities, the production in Germany and France, for instance, during 1910, amounting to about 5000 tons for each country. To date this product has been obtained only as a by-product in the manufacture of glue, *i.e.*, in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bicalcic phosphate is obtained.

On the other hand, it is a long while ago since it was first proposed to obtain bicalcic phosphate as the chief product from every kind of raw phosphate in the same way, viz., by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it does not contain too large a proportion of any useless soluble compound, such as carbonate of lime. In the production of acid phosphate, on the other hand, one can not utilise raw phosphate with a lower percentage than about 50 per cent bone phosphate, since owing to the admixture of gypsum the percentage in the acid phosphate of available phosphoric acid is only about half that of the raw phosphate's percentage of phosphoric acid, and consequently consideration of freight charges for the prepared article excludes the use of a raw material in which the percentage is low.

However, it has been found that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance, perchlorate of sodium, is electrolysed with a diaphragm, so that free acid is generated in the anode chamber and a solution of caustic alkali in the cathode chamber. With an electrolysing tension of 4½ volts and 80 per cent current efficiency it is easy to calculate that in order to produce the kilogrm. equivalent of acid 182 horse-power hours are required, whereby the alkali necessary for the precipitation of the bicalcic phosphate is obtained at the same time without additional cost in the cathode chamber. If we assume that one electric horse-power can be obtained for 10 dols. a year—the usual price in many parts of Europe, and presumably in many places in America—then the cost of the equivalent of 1 kilogrm. of acid amounts to about 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling, &c., as the electrolyte regenerates, as will be seen from what follows.

If we assume that the price of 1 ton of chamber acid with 65 per cent H_2SO_4 is 5 dols., we shall find that the cost of the kilogrm.-equivalent of H_2SO_4 (49 kgrms.) is about 38 cents.

This calculation consequently shows that provided the remaining outlay for the electrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilisation of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try to make the method economically feasible, chiefly by finding a suitable electrolyte, and by constructing a serviceable electrolyser.

As in the process there is no consumption of chemicals, beyond loss by spilling, &c., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the method depends therefore in the first place on the price of the power.

Before entering upon detailed descriptions a general survey of the method will be of advantage.

General Features of the Method.

In an apparatus expressly constructed for the method, a solution of chlorate or perchlorate of sodium is electrolysed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains one-third of the lime originally

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dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means, and again enters the electrolysing apparatus.

Of course the hydrogen, obtained as a by-product at the cathode in the electrolysis of the salt solution, could be used for making ammonia or in any other way, thus increasing the value of the products obtained.

The Nature of the Electrolyte.

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance, chlorides, being of no account. Both these salts can now, since they are being produced by electrolysis, be had at reasonable prices. Nitrate of sodium cannot be used because it is too strongly reduced at the cathode to nitrate, ammonia, &c.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolysing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber, and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonic oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as occur in the electrolysing (maximum, 50° C.). Furthermore, the salt is exceedingly easily soluble (deliquescent), and thus easy to wash away.

Chlorate of sodium is less constant in that the chloric acid solution formed in the anode chamber already begins to decompose at 40° C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate there is oxidised to perchlorate. For this reason a start can very well be made with chlorate of sodium, since, though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they soon disappear, viz., when the chlorate has become perchlorate of sodium. Even if you begin with chlorate of sodium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher than at about 1 per cent of the weight of the bicalcic phosphate developed.

Another way of carrying out the process is this:—A solution of chloride of sodium is electrolysed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid, wherewith the raw phosphate is dissolved, whereupon a precipitate is formed with this caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process, by several reasons (depreciation of anodes, loss of chlorine, &c.), is not so advantageous.

The Electrolysis.

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphragm. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I cannot enter into details.

The voltage has been found to amount on the average to 4·5 volts per cell, including loss in connections. It varies somewhat, depending on the age of the diaphragms, the efficiency of the electrical contacts, and the temperature of the solutions, which may vary at different times of the year; but, as stated, the average voltage is 4·5. The polarisation amounts to 2·97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali or perchloric acid), the current efficiency continually diminishes, of course, in proportion as the newly formed substances begin to take part in the current circuit. We generally produce solutions with 1 grm.-equivalent of acid or alkali per litre, and have then a current efficiency of 82 per cent and a ballast of undecomposed salt in both acid and alkali solutions.

The Raw Material and its Utilisation.

Of course, the high percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need only mention in illustration low percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron ore, and certain low percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bicalcic phosphate from the solution, the product obtained will always be of the same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20 and 88 per cent.

Furthermore, the raw phosphate need not be finely pulverised, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity. We have worked with material of as coarse crushing as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula—

$$Ca_3P_2O_8 + 6HClO_4 = 3Ca(ClO_4)_2 + 2H_3PO_4,$$

then per litre of normal acid 23·7 grms. of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction in contrast, for instance, to the reaction $CaCO_3 + 2HClO_4 = Ca(ClO_4)_2 + H_2O + CO_2$ will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon dioxide. We have also found that we must reckon with a somewhat lower figure, say, 20 grms. P_2O_5 or 43·6 grms. $Ca_3P_2O_8$ per litre of normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphoric acid (P_2O_5) is 23·7, and for carbon dioxide (CO_2) 22, we can consequently state that 1 per cent of CO_3 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1 per cent of P_2O_5, without giving any product of any value to speak of (the amount of carbonate of lime obtained as a by-product will, of course, be correspondingly greater). A raw phosphate which contains 20 per cent of P_2O_5 (as $Ca_3P_2O_8$) and 2 per cent of CO_2 (as $CaCO_3$) consequently requires about 10 per cent more energy than a raw phosphate with the same proportion of phosphoric acid, but free from carbonate of lime.

Iron oxides (iron ores), on the other hand, are only dissolved very slightly. We found that after twenty-four hours' shaking at the usual temperature with normal acid there was dissolved of magnetite a quantity corresponding to 0·24 grm. Fe_2O_3 per litre from hematite, a quantity corresponding to 0·20 grm. of Fe_2O_3 per litre, which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids. However, silicates may occur, for instance, together with apatite, which are so easily soluble that they dissolve to a noticeable degree if the acid is in contact

with them for any length of time after most of the phosphate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilisation of the bone phosphate in the raw material, we can as a rule count upon extracting 98 per cent of it, sometimes more, sometimes a little less, viz., when easily soluble silicate is present.

Precipitation of the Bicalcic Phosphate and Calcium Carbonate.

To precipitate the bicalcic phosphate we made use, as before stated, of the solution of caustic soda obtained by electrolysis and saturated afterwards by carbonic acid, which is introduced into the phosphate solution by means of a sprayer.

The employment of the soda solution as a precipitant, instead of milk of lime, has a considerable advantage. For the fact is that as soon as the solution has become alkaline at any point, bone phosphate is precipitated there instead of bicalcic phosphate. This once precipitated bone phosphate is only slowly converted into bicalcic phosphate, even if the average acidity of the liquid is such that only bicalcic phosphate ought to occur. At least a portion of the bone phosphate thus formed remains therefore in the precipitated bicalcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2 per cent citric acid ; but it has no fertilising value worth speaking of. The phosphoric acid precipitated as bone phosphate must therefore be looked upon as lost.

Now, it is clear that it would he much easier to avoid the formation of bone phosphate if a sodium-hydrate solution, distributed in jets, were employed as the precipitant than if milk of lime was used, since in the latter case we get particles of solid calcic hydrate, round which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution remains very slightly acid or only just neutral, bicalcic phosphate can be precipitated so completely that only 0·1 to 0·2 per cent of all the phosphoric acid remains unprecipitated, while 98 per cent of the phosphoric acid in the bicalcic phosphate is soluble in citrate, and thus only 2 per cent of the phosphoric acid is present as bone phosphate.

The precipitated bicalcic phosphate, which is microcrystalline, is filtered off, washed, and dried. It thus forms a light pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to 35 to 38 per cent, according to the completeness of the drying.

If we call to mind that about 2 per cent of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2 per cent is recovered as precipitated bone phosphate, we shall find that about 96 per cent of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bicalcic phosphate obtained shows, even if it contains iron and aluminium phosphate, no falling off of soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, deterioration shows itself in damp acid phosphate. The following analyses may be quoted to show that such degeneration does not occur : —

	Total P_2O_5 per cent.	Citrate-soluble in	
		P_2O_5 per cent.	P_2O_5 in per cent of total P_2O_5.
Fresh	35·45	34·58	97·54
After 3 months	36·02	35·13	97·53
After 6 months	36·54	35·72	97·95

From the filtrate of the bicalcic phosphate is precipitated, as we have already mentioned, the lime that remains in the solution, together with the rest of the sodium hydrate solution, after the latter has been saturated with carbonic acid from fuel gases as carbonate of lime, which can be used as a fertiliser or in chemical workshops.

Its mass corresponds to about one-fourth of the weight of the bicalcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

Power Expenditure.

From the statements given above it is easy to calculate what electric horse-power (direct current) produces per year of $350 \times 24 = 8400$ hours; it will work out at 2·24 tons of bicalcic phosphate with 35 per cent of citrate-soluble phosphoric acid, if free of carbonate. If a 38 per cent article is produced, $\frac{2{\cdot}24 \times 35}{38} = 2{\cdot}06$ metric tons per horse-power year will be obtained, &c. The production with carbonaceous raw product has been stated above.

Value of Bicalcic Phosphate Fertiliser.

Careful experiments extending over many years have been made, partly by Prof. H. G. Söderbaum, Agricultural Chemist at the Central Institution for Experimental Agriculture, Stockholm, partly by Dr. Hj. von Feilitzen, Director of the Swedish Peat Society, Jönköping, Sweden. Prof. Söderbaum's earlier investigations are reported in "The Experiment Station Record," edited by the United States Department of Agriculture, Washington, vol. xiv., No. 10, 1903, pp. 951 2, and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calciumphosphat" in the *Zeitschrift fur das landwirtschaftliche Versuchswesen in Oesterreich*, 1908, pp. 506—10. Dr. von Filitzen has communicated the chief results of his investigations in the *Journal fur Landwirtschaft*, 1910, pp. 33—43.

As Dr. von Feilitzen is going to give an account of his further investigations at the Congress, I will here only briefly mention the chief result of his and Prof. Söderbaum's culture trials.

The result of the experiments in cultivation is that the citrate-soluble phosphoric acid in the bicalcic phosphate proves to possess the same fertilising value as the water-soluble phosphoric acid in the superphosphate, and consequently the same value as a trade product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bicalcic phosphate through the agency of the compounds of lime present there. This result is supported by the trials carried out by practical agriculturists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage the freight charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle, and does not damage the sacks in the least.

The Superior Advantages of the Electrolytic Method.

The merits of the electrolytic method are as follows :—

(*a*) It admits of the use of cheap low percentage raw phosphate not available for the superphosphate nor available for the superphosphate industry.

(*b*) By it a phosphate containing 35 to 38 per cent of soluble phosphoric acid is obtained even from low percentage raw material.

(*c*) Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

(*d*) Retrogradation of soluble phosphoric acid when stored does not occur.

(*e*) The raw phosphate need not be reduced to a finely powdered state.

(*f*) Bicalcic phosphate can be employed as a fertiliser on all kinds of soil, even on sandy and boggy land.

(*g*) Bicalcic phosphate will be of excellent use in the manufacture of "complete fertilisers."

(*h*) Sacks are in no wise damaged by the product.

(*i*) The product is a finely divided white powder which s easily spread on the field.

The process is now being carried out in a small factory, the first factory belonging to the Difosfat Company, Trollhättan, Sweden.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The F-rays.

The scientific world has been somewhat startled by the sensational discovery announced by the newspapers that an Italian physicist, Ulivi, had discovered the means of capturing or manufacturing artificially the infra-red rays of the solar spectrum, and of directing them at will, at a distance of more than 20 kilometres. After the discovery of so many radiations with which we are already acquainted—the X-rays, the α-rays, β-rays, γ-rays, after the Hertzian radiations which exist; and the hypothetical radiations, the N-rays of Prof. Blondlot, the N-rays of Major Darget—we have now the F-rays.

For the F-rays is the name that Ulivi has given to the infra-red rays that he has been able to produce artificially. The radiations would seem to have the property of being able to make certain explosives, such as dynamite, melinite, lyddite, pyroxylin powders, explode at a distance spontaneously, if only these diverse matters are in contact with a metallic armature.

To the west of the Havre roads in front of the sea-side place of Villiers, M. Ulivi has gone through a series of experiments before a certain number of important person ages of the French war ministry. Some submarine mines had been placed at distances of 600 metres apart over a distance of 6000 metres. M. Ulivi directed the cone of the parallel waves of his F-rays on to these different floating mines. They blew up with marvellous precision, one after the other. We have no other information concerning M. Ulivi's discovery, which, if it is confirmed, may have most formidable and unexpected applications. The fact that superior officers of the French staff and Captain Ferrie, whose numerous works on wireless telegraphy are well known, were present at these different trials, is a proof of the reality of the discovery. It is not known, however, whether it is a calorific or electric phenomenon which brings about the explosion of the cartridges, torpedoes, and fortified casemates containing the ammunitions.

Why have We been having Cold Weather last Summer and this Summer?

Meteorologists have noticed that the average temperature of last summer was more than 2° lower than the normal average of the hot summer months. In France, in England, as well as in Central and Eastern Europe the summer was very sensibly cool. It was not known whether this unexpected coolness was to be attributed to an extra important breaking-up of the Arctic ice, or to a series of winds coming from the north, though no explanation was forthcoming of this phenomenon, from a meteorological point of view.

Measures taken at the Pic du Midi, the Puy de Dôme, the Brocken, in fact everywhere in Europe, showed an unusual retrogradation of the temperature from the middle of July. In the United States, in Australia, in Africa, the same facts were remarked, so that it was proved that the phenomenon was general, and the famous law of compensation did not apply itself to the occasion.

Messrs. Abbot and Towle observed, the former in Algeria, the latter at the Observatory of Mount Wilson, that from June 12, 1912, a marked decrease in the solar radiance had taken place. The transparency of the air seemed to be slightly obscured, so that the heat received from the sun was inferior, by a fifth, to its average value for the same season.

The cause was perfectly simple; a veil of microscopic dust had spread itself over the sky and kept back from the earth a part of the heat transmitted by the sun. This dust, disseminated in the air by aërial currents, came from a terrible eruption that had taken place at the volcano of Katmai in Alaska. This eruption began on June 6, 1912, and only stopped on the morning of the 7th. The fall of volcanic dust was so great that a layer of more than 12 cm. thick was deposited on the deck of a ship that was in those parts. On the shore the thickness of the ashes was more than 30 cm. As a simple indication, it may be mentioned that the dust deposited by the eruption of Krakatoa was not, at the same distance, more than 2 cm. thick.

It is, then, highly probable that it is to the eruption of Katmai that is due to the cold summer of last year, and it is probable that the summer of 1913, which it would seem is likely to be be equally as cool, is suffering also from the ashes still floating in the atmosphere, and which are stopping a part of the calorific radiations of the sun.

The Deformation of Bodies subjected to Strain.

Lieut.-Col. Hartmann is contributing his experimental researches concerning the deformation of solid bodies subjected to strain.

Trials have been undertaken to determine the individual modification that the grains of metals undergo in the deformed regions, according to the place they occupy.

The learned artilleryman has likewise studied the mechanism by which permanent deformations produce the increasing augmentation of resistance up to a determined value of the charge, so that he has particularly tried to bring into notice molecular tensions that are brought into existence by their deformations.

In a second series of experiments Col. Hartmann has specially studied the geometrical puckering that exterior actions produce in matter. Methodical trials have been effected with metallic tubes compressed between two parallel planes, with a view of completing the first results previously obtained, thanks to a very great variety in the dimensions as well as in the preparation of the pieces experimented upon.

The cinematograph has been employed in the most interesting cases, to obtain successive images of deformation at instants very near to each other. Moreover, the study has been extended to bodies of various forms, and to diverse kinds of strain. These last researches are not yet completed; those which are at present being pursued seem likely to supply the explanation of the phenomenon of the regular distribution of the puckering; the interest of which is so much the greater since it brings into play the elastic properties of matter that are frequently observed in nature.

The Production of Carbide of Calcium.

The world's production of carbide of calcium is progressing. According to the latest statistics published by the *Journal of the Electric Kiln and the Electrolysis* it reached 300,000 tons in 1912. This progress is due, not so much to the development of the applications of acetylene as to the continually increasing extension of the manufacture of cyanide, used as a manure in agriculture.

In Europe it is Germany that holds the record for the consumption of carbide. In 1911 she imported 37,000 tons, and 48,000 in 1912; the exportations nil. Sweden is the country that manufactures the most carbide and that consumes the least. The factories of Odda are provided with the means of manufacturing 80,000 tons of carbide of calcium for the preparation of manure. In 1912 Switzerland exported 5 million francs worth of carbide. Austria-Hungary also exports nearly 11,000 tons per

annum. England, on the contrary, only imports quantities of carbide varying between 14,000 and 18,000 tons, As for France, her importations during the years 1910, 1911, 1912 were respectively 445, 2162, 3302 tons; the exportations were 4824, 5058, 6225 tons. It is especially the development of lighting by acetylene gas in the French colonies that has increased so regularly the figures of exportation.

Coloured Photography on Tissues.

Messrs. Valette and Feret, of the National Gobelin Tapestry Manufactory, have recently explained to the Society of Encouragement of National Industry, a remarkable process of their invention destined to reproduce on tissues decorative effects that up till now have never been attained by any process. It is an application of trichromy to tissues. The proofs are obtained by three successive printings, blue, yellow, red, from three selected photographic clichés. The tissue is rendered sensitive by the help of diazoic sulphates mixed with alkaline phenyl products, which have the property of producing colouring matters only under the influence of light.

The indispensable adjustment for the precise superposition of the three printings is effected by means of a special frame with notches. This adjustment may be performed with great exactness, in spite of successive manipulations. The applications of this process are the same as those of printed tissues in general, but more especially for rich articles of a limited number, and which it is difficult to execute by machine, such as tapestries, hangings, fans, sachets, reproductions of pictures, and even of portraits taken from life.

NOTICES OF BOOKS.

A Text book of Rand Metallurgical Practice. By Ralph Stokes, Jas. E. Thomas, G. O. Smart, W. R. Dowling, H. A. White, E. H. Johnson, W. A. Caldecott, A. McA. Johnston, C. O. Schmitt. Volume I. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

No better proof could be adduced of the great value of this book than the fact that the first large edition of it was exhausted within twelve months of its publication, and the high opinions expressed of its merits have been fully justified. Very few changes have been made in the second edition, beyond some corrections of small errors and the amplification of some of the tables and statistics.

Chemistry. By Georges Darzens. London: Constable and Co., Ltd. 1913.

This book is one of a series of monographs called "Thresholds of Science," which was first published in France; it is presumably a translation, although no mention of a translator is made on the title page. In the first part of it easy experiments are described, such as could be performed with simple apparatus in an ordinary room or a very meagrely equipped laboratory. These experiments are intended to illustrate the elementary principles of physical and general chemistry and the laws of chemical combination, and to give some knowledge of the properties and reactions of the more important elements and compounds. This part of the book does not differ materially from the usual type of text-book of elementary chemistry intended for beginners. The section which deals with applied chemistry gives interesting short accounts of metallurgy, the manufacture of glass, soap, perfumes, &c., and describes some rather unusual experiments which are sure to arouse the interest of the young student.

Disinfection and Disinfectants. By M. Christian. Translated from the German by Charles Salter. London: Scott, Greenwood, and Son. 1913.

Modern methods of disinfecting are very thoroughly and systematically treated in this book, which gives an admirable account of the results which have been obtained by the scientific study of this branch of hygiene. Physical methods of disinfecting are first discussed, including treatment by dry heat, steam in various conditions (superheated, under pressure, &c.), light and other rays, electric currents, and mechanical influences. Different types of apparatus for the purpose are described and illustrated, and some methods of sterilising food, such as the pasteurisation of milk, are included. The second part of the book deals with chemical disinfection, and gives succinct directions for its practical application. The various reagents are grouped according to their chemical natures, and the strength and efficacy of many patent preparations are discussed. Different methods of disinfecting rooms without apparatus are included, and a chapter on combined methods of disinfection brings to a conclusion a thoroughly scientific account of the most recent methods of preventing the spread of diseases.

Livingstone College Year-book. Centenary Number, 1913. Livingstone College, Leyton, E.

This report of the work, aims, and objects of Livingstone College contains a short account of the progress made in Tropical medicine during the year 1912, and, although no very startling discoveries have been made, much valuable research work has been done, especially on sleeping sickness and the treatment of dysentery. Some important books on tropical medicine and hygiene which have recently appeared are shortly reviewed, and brief notes on new drugs and preparations which have been placed on the market are added.

CORRESPONDENCE.

SWEDISH TAR AND WOOD BY-PRODUCTS.

To the Editor of the Chemical News.

Sir,—In enclosing a copy of our Special Tar and Wood By-product Number we beg to state that any of your readers interested in the wood tar and allied trades can receive, post free, a copy of this publication by writing to us, mentioning the notice to this effect, which we trust you will kindly insert in your esteemed Journal.—I am, &c.,

Louis Zettersten, Secretary.
For the Swedish Chamber of Commerce in London.

Literary Intelligence.—Amongst the new scientific books to be issued in the autumn by Messrs. J. and A. Churchill are the following: — "Industrial Organic Analysis" (For the Use of Technical and Analytical Chemists and Students), by Paul S. Arup; with a Foreword by Dr. J. C. Irvine, Professor of Chemistry at the University of St. Andrews. "Quantitative Analysis in Practice" (an Introductory Course designed for Colleges and Universities), by John Waddell, Assistant Professor of Chemistry, School of Mining (Queen's University), Kingston, Canada. "Bloxam's Chemistry, Inorganic and Organic," Tenth Edition, thoroughly revised by A. G. Bloxam and Dr. S. Judd Lewis; many new illustrations are added. "Practical Chemistry" (Qualitative Exercises and Analytical Tables for Students), by the late J. Campbell Brown, Professor of Chemistry, University of Liverpool; Sixth Edition, Revised by Dr. G. D. Bengough, Lecturer on Metallurgy, University of Liverpool. "Dental Anatomy," Human and Comparative, by C. S. Tomes; Seventh Edition, Revised by Dr. Marett Tims and A. Hopewell-Smith. A radical revision has been undertaken, both as regards the text and the illustrations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 23, June 9, 1913.

Reactions between Water and Sulphurous Acid at Various Temperatures. Formation of Hydrosulphurous Acid.—E. Jungfleisch and L. Brunel.—Water and sulphurous anhydride react at temperatures below 160° and even at the ordinary temperature. The reaction is slower the less concentrated the sulphurous solution is and the lower the temperature. About 160° the transformation produces sulphur and sulphuric acid, which are the ultimate terms of the reaction. Their formation takes place in two stages. In the first, hydrosulphurous and sulphuric acids are formed, and in the second stage the former splits up into sulphur and sulphuric acid. These transformations appear to be accompanied by secondary reactions.

Use of Calcium Carbonate as Catalyst for Organic Acids and Anhydrides.—Paul Sabatier and A. Mailhe.—The transformation of organic acids into acetones can readily be effected if precipitated calcium carbonate is used as catalyst, and this method of preparing propanone and diethyl ketone is very convenient. The anhydrides of the acids undergo a similar reaction.

Synthesis of Carbon Oxycyanide by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—Mixtures of CO and C_2N_2 were exposed in quartz tubes to the mercury lamp light for twelve hours. After about a quarter of an hour a yellowish red deposit of carbon oxycyanide was seen on the cold part of the tube. From the change of volume which occurs it appears that the composition is CN.CO.CN. The solid oxycyanide when heated to 200° does not volatilise, but gives up small quantities of oxygen. It is soluble in alkalis. With water it undergoes the following reaction: $CN.CO.CN + HOH = CO_2 + 2HCN$.

Quantitative Separation of Iron and Chromium.—F. Bourion and A. Deshayes. Chromium oxide can be separated from iron oxide by a method based upon the insolubility in water of anhydrous chromic chloride. The mixture of oxides is subjected to the action of a slow current of chlorine containing sulphur chloride vapour, the temperature being gradually increased from 200° to 650°. This method can be recommended for mixtures which are poor in chromium, and also for mixtures of any composition, provided that the oxides have been calcined.

Constitution of Paramolybdates and Paratungstates.—H. Copaux.—Sodium molybdoaluminate is best represented by the formula $[Al(Mo_2O_7)_3]Na_3 + Aq$, which is derived from the orthoaluminate, AlO_3N_3, by the substitution of three divalent radicals, Mo_2O_7, for three atoms of oxygen. Molybdic anhydride, MoO_3, corresponds to an orthomolybdic acid, MoO_6H_6, the salts of which are unknown in the free state, but become stable by the introduction of Mo_2O_7 radicals. If three oxygen atoms are thus replaced the formula $\left[\begin{matrix}Mo.(Mo_2O_7)_3\\O_3\end{matrix}\right]M_6 + Aq$ is obtained (M being a monovalent metal). This represents the paramolybdates, which are substituted orthomolybdates in which the molybdenum plays two parts, that of generator of acid and substituent. The paratungstates the author represents by the formula $[H(Wo_2O_7)_3]M_5 + Aq$. The study of the absorption of light and the dehydration under the action of heat confirms these formulæ.

Derivatives of β-Methylcyclopentanone.—Marcel Godchot and Félix Taboury.—When dry chlorine acts on β-methylcyclopentanone in diffused light at a temperature not exceeding 25°, β-methyl-α-chlorocyclopentanone is formed. This is hydrolysed by water, giving a methylcyclopentanolone, which on oxidation yields α-methylglutaric acid. β-Methylcyclopentenone is also formed by the hydrolysis of the chloro compound.

Preparation of Diglyceric Alcohol.—Jean Nivière.—To prepare diglyceric alcohol equimolecular proportions of glycide and glycerin are heated on the water-bath for six or seven hours. The mixture is then acetylated by boiling with acetic anhydride, and the tetraacetine which is obtained between 195—205° under 1 to 2 mm. pressure, is saponified with alcoholic soda. The alcohol is a yellowish very viscous liquid, which is insoluble in ether, soluble in water and alcohol, and hygroscopic like glycerin.

Vol. clvi., No. 24, June 16, 1913.

Ketimines.—Charles Moureu and Georges Mignonac.—Ketonic imines which contain the divalent reside =NH may be called ketimines. To prepare diphenylketimine, $C_6H_5-C(=NH)-C_6H_5$, a compound is first made of benzonitrile and phenyl magnesium bromide. It is washed with ether and mixed with ammonium chloride. Decomposition occurs, and all the magnesia dissolves. The whole is then shaken with ether, and the ethereal liquid is dried over anhydrous sodium sulphate and saturated with dry hydrochloric acid gas. The ketimine is thus precipitated as hydrochloride. This is a general method of preparing ketimines in which the residues attached to the functional group are aromatic; it can also be applied to the case of the mixed fatty aromatic ketimines, which, however, are more easily decomposed by water. The ketimines are usually oils or solids of low melting-points. They are basic substances giving crystalline salts, and are unsaturated. The ketimine function appears to be very active, and takes part in many reactions.

Bromination of Secondary Hydroaromatic Ketones and Alcohols.—F. Bodroux and F. Taboury.—The authors have already shown that the bromination of cyclohexanone and cyclohexanol in carbon tetrachloride solution gives the same compound, a tetrabromocyclohexanone. The same process applied to some homologues of this ketone and alcohol gives similar results, a tri- or tetrabrom derivative being obtained. These derivatives are not very stable, and at a temperature a little above their melting-point they decompose into bromine, hydrobromic acid, and brominated phenol. The same transformation occurs slowly under the influence of light at the ordinary temperature.

Quantitative Study of Absorption of Ultra-violet Rays.—Jean Bielecki and Victor Henri.—The authors have investigated the absorption of the ultra-violet rays upon the following substances:—Primary, secondary, tertiary amines, diamines, nitriles, carbylamines, amides, ketoximes, and aldoximes. They find that the value of ε increases regularly as λ diminishes, down to 2144. The absorption by the amines increases with the number of carbon atoms contained in them. When the hydrogen atoms of ammonia are replaced by radicles C_nH_{2n+1} the absorption increases very rapidly. Substances containing a nitrogen with a triple bond or those in which nitrogen is pentavalent absorb very little. The amides behave like the corresponding acids, thus the substitution of the NH_2 group increases the absorption, and the absorption by the oximes is less marked than that of the amines.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 12, 1913.

Catalytic Hydrogenation of Methylcyclopentanones.—Marcel Godchot and Félix Taboury.—β-Methylcyclopentanone when subjected to the action of hydrogen at 150° in presence of reduced nickel gives a liquid which can be separated into two fractions by distillation. The first, which comes over between 140° and 150°, consists chiefly of β-methylcyclopentanol, while the second portion, distilling between 244° and 246°, consists of the ketone β3-dimethylcyclopentylcyclopentanone. The reaction in the case of α-methylcyclopentanone is analogous, the chief product being again the double ketone.

THE CHEMICAL NEWS.

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(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Lees Reader in Chemistry—(Vacant).

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A., F. D. Chattaway, M.A., D.Sc.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: A. Angel, M.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M.A. Queen's College Laboratory: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University, either by examination or by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—H. Krall, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 4th.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(UNIVERSITY OF LONDON).

Senior Professor of Chemistry—J. M. Thomson, LL.D., F.R.S.

Professors — Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., Thomas Wright, B.Sc., and E. W. Skelton, B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1913-1914 are Oct. 1, Jan. 14, and April 29.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants—R. W. Gray, Ph.D.; S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Tuck, D.Sc.; Irvine Masson, M.Sc.

The Session is divided into three Terms, as follows:—First Term, from September 30 to December 19; Second Term, from January 13 to March 27; Third Term, from April 28 to June 15.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt, ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen-fixation; and other technical processes.

Junior Course of Inorganic Chemistry.

The more important inorganic substance will be dealt with. Special attention will be paid to general points of view, and to the application of physico chemical laws and methods.

First and Second Terms: The Class meets three times a week, on Mondays, Wednesdays, and Fridays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays and Fridays at 9 and another hour to be arranged.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Courses of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to July: Tuesday and Thursday at 9.

The Courses comprise Stoichometry, the Liquid and Solid States of Matter, the Phase Rule, Thermochemistry, and in general the Application of Physical Methods to the Solution of Chemical Problems, Chemical Statics, the Electrolytic Dissociation Theory, Chemical Dynamics, and Chemical Thermodynamics.

Fees:—Courses, £5 5s.; Term, £2 2s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry—W. A. Bone, F.R.S.

Assistant Professors—M. O. Forster, Ph.D., D.Sc., F.R.S.; J. C. Philip, M.A., Ph.D., B.Sc.; B. Mouat Jones, M.A.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) will be awarded in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their courses. Three Research Fellowships, founded by Mr. Otto Beit, of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of Universities in the United Kingdom.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 72nd Session will commence on Oct. 1, 1913.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—A. Brooke, Ph.D. (Strassburg).

Lecture Assistant—W. Beynon Williams, B.Sc.

Student Assistant—William Thomas, B.Sc. (Wales).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1913-1914, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 16, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Pros-

pectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, Alice E. Smith, D.Sc., J. O. Hughes, B.Sc. Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens September 30th, 1913. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Science Degree Course taken in one year, £4 4s.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constitutent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor in Metallurgy—A. A. Read, M.Met., F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

A course on Inorganic Chemistry will be given in the Session 1914—1915.

The following lectures on Metallurgy will be given by Prof. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held. Practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

DEPARTMENT OF CHEMISTRY.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Inorganic and Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electrometallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

DAY LECTURES.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work.

3. Physical Chemistry—Two Lectures per week for two Sessions and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—Intermediate Science—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened, for students who have attained the standard of an Inter. B.Sc. examination, from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Second year Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, D.Sc., B.A., F.I.C., F.C.S.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.
Demonstrators—E. G. Moody and H. Orr.
Assistant in Chemical Laboratory—R. K. Lloyd.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 22nd.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators — Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, D.Sc.; J. E. Coates, M.Sc.; E. P. Frankland, Ph.D., B.A., M.Sc.; Ernest Vanstone, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 7th, 1913.

The Chemical Department is housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9 30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*—This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc., F.I.C.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; N. Bland, M.Sc; A. Jackson, B.Sc.; S. F. Stell, F.C.S.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturers in Dyeing—A. B. Knaggs, F.C.S.; M. Fort, M Sc.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Past Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. A completely equipped Practical Dyehouse and Finishing Rooms have now been added.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—H. Douglas Elkington, B.Sc., A.I.C.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc, Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc., F.I.C.; J. Marshall, M.Sc.; H. S. Patterson, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry. — (A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry. — (B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee. £4 10s.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon; fee, £4 10s. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (*d*) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S. F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.

Demonstrator—A. Woodhead, M.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—E. Stiasny, Ph.D.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livesey Professor—J. W. Cobb, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. J. Hodsman, M.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Bio-chemistry—Benjamin Moore, M.A., D.Sc., F.R.S.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Guy D. Bengough, D.Sc., M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—A. J. Allmand, D.Sc.; F. D. Farrow, M.Sc.; Francis W. Kay, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froysell.

The Session commences October 7th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic, Physical, and Bio-chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L—Applied Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1913, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.
(IN THE UNIVERSITY OF DURHAM).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Demonstrators—A. Foister, M.Sc., Ph.D.; A. S. Blatchford, B.Sc.; and W. Wardlaw.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—G. S. Robertson, B Sc.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 9 h. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(*a*) Inorganic Chemistry.—Advanced Course, Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(*b*) Organic Chemistry.—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*c*) Organic Chemistry.—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*d*) History of Chemistry and Chemical Philosophy.—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*e*) Physical Chemistry.—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*f*) Analytical Chemistry.—Fridays at 9.15 a.m. Fee, £1.

(*g*) The Rarer Elements and the Periodic Law.—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the course *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses, *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M.; G. H. S. Kent. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) Ancient History, (*e*) French, (*f*) German, (*g*) some other language to be approved, (*h*) Experimental Science or Physics or Chemistry, (*i*) Botany or Zoology, (*j*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting therefrom, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the

Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 2nd, 1913. Candidates should send in their names to the Secretary on or before September 12th.

Evening Lectures.—Under the auspices of the College and the Newcastle Section of the Society of Chemical Industry, special Courses of Evening Lectures will be given—Course of 5 Lectures by Prof. Cobb, Fuel Economy, to commence in October 1913, and a Course of 5 Lectures commencing January, 1914, to be announced later.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 30th. Candidates should send in their names to the Secretary on or before September 22nd.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc, Ph.D., F.R.S.

Professor of Organic Chemistry — Arthur Lapworth, D Sc, F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; E. C. Edgar, D.Sc.; and F. P. Burt, D.Sc.

Assistant Lecturers and Demonstrators—F. R. Lankshear, B.A., M.Sc.; Edward Hope, M.Sc.; J. E. Myers, M.Sc.; Jacob Jones, M.Sc.; and J. R. Partington, M.Sc.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Assistant Lecturer in Metallurgy—J. H. Andrew, M.Sc.

Lecturer in Electro-Chemistry—J N. Pring, D.Sc.

The Session begins October 1st, 1913.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters — Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry

Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.; J. Kenner, Ph.D., B.Sc.

The Session will commence October 1st.

Matriculation Course. — Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B.Sc. Course in Chemistry.—Monday at 9.30 a.m. and Tuesday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 a.m., during two terms, Thursday at 10.30 a.m. and Friday at 10 30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

Lecturer—J. H. Wreaks, B.Met.

Lecturer in Non-ferrous Metallurgy—G. B. Brook.

Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected. but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character.

Working accommodation is provided for 30 students at one time, and the course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students. provide the means for the Chemical examination of the alloys prepared. A Staff and Post-graduate research laboratory completes the provision for the chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ross microscopes. The recalescence laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Colver-Glauert Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph.D., D. ès Sc., F.I.C.

Lecturers—J. W. Dodgson, B.Sc.; A. E. Everest, M.Sc.

Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D., F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for studen s preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hall, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.

Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The Junior Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First Professional).

The Intermediate and Advanced Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Technological Work or Research.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.

Demonstrators—Joseph Knox, D.Sc.; W. H. T. Williamson, B.Sc.

I. *General Lecture Course* (100 *Lectures*).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Physical Chemistry* (60 *Lectures*).—Three Lectures a week on Physical Chemistry, with Practical Demonstrations, are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. *Inorganic Chemistry* (40 *Lectures*).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

V. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; Alfred Hill, B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological

Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc., and six Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; F. D. Miles, B.Sc.; and Clerk Ranken, D.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Analytical and Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University of Edinburgh as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Day Classes open on October 7th, and the Evening Classes on September 29th.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 23.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by attendance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1913-1914 may be had from the Director, Mr. H. F. Stockdale,; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Salvator and St. Leonard

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £50 to £10 each per annum, will be held on September 12th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees.; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily ; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises :—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry ; (2) Qualitative and Quantitative Analysis ; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts. Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—*Advanced Chemistry.*—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—*Practical Chemistry for Engineering Students.*—A special course is given during the third term. Fee, £3 3s.

V.—*Laboratory Pupils.*—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m. —5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics :—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

UNIVERSITY COLLEGE, CORK.

A Constituent College of the National University of Ireland.

Professor—Augustus Edward Dixon, M.D.
Assistant Lecturer—John Taylor, M.Sc.
Demonstrator—James L. McKee, B.A., Ph.D.

The College Session will commence in October, 1913, and end in June, 1914. All classes are open to male and female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.

2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.

3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.

4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.

5. Courses in Systematic and in Practical Chemistry for Students of Engineering.

6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

University College, Galway.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Robert B. Forster, Ph.D., and Miss R. Clarke, B.A.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple gravimetric quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses* —Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—First Year's Course. — Same as Faculty of Science.

Faculty of Medicine.—First Year's Courses.—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates, and the chemical examination of urine. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—First Year's Courses.—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, first year.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION

(F.I.C. and A.I.C.).

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to elevate the profession of Chemistry, by setting up a high standard of scientific and practical proficiency for persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers, by examining Candidates, and granting certificates of competency, and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance

with the Regulations of the Institute : (i.) Higher Physics ; (ii.) Advanced Mathematics ; (iii.) Mechanics and Chemical Engineering ; (iv.) Metallurgy ; (v.) Geology and Mineralogy ; (vi.) Physiology ; (vii.) Bacteriology ; (viii.) Agriculture ; (ix.) Elementary Botany ; (x.) Elementary Biology ; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associateship* (*A.I.C.*).—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry ; metallurgical chemistry ; physical chemistry ; organic chemistry ; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water ; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship* (*F.I.C.*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute—The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. Programmes of the London Colleges may be had on application to the Temporary Offices during the rebuilding of Gresham College, Leonard Street, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds* (*Engineering*) *College, Exhibition Road.*—The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops ; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers ; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works ; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions : Day Classes for those who are able to devote one, two, or three years to systematic technical education ; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Classes and Laboratory Practice in Chemistry, Botany, and Geology, open to Students of both sexes. Day Commercial School.

Battersea Polytechnic.—Principal, S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, Bacteriology, Materia Medica, Paper Making and Testing, Oils and Fats, Dyeing, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in various Technical subjects. (For further information see College Calendar).

Borough Polytechnic Institute, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Dorée, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro chemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see College Calendar).

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 29. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

Northern Polytechnic Institute, Holloway Road, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of

Education examinations. Prospectus sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street, E C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

South Western Polytechnic Institute, Chelsea.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of four years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 3½d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S. Lectures and Practical Classes are held, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to Research and Post-graduate studies. Evening Classes for London University Degrees are also held.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R. S. Willows, M.A., D.Sc., H. Burrows, A.R.C.S., Ph.D., F.I.C., G. F. Morrell, B.Sc., Ph.D., &c., G. Senter, D.Sc., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., M.I.M.M., G. Patchin, A.R.S.M., Wesley J. Lambert, Assoc.Inst.C.E., Arthur Harden, D.Sc., F.R.S., &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Harlow, B.Sc., &c. The new Session of the Sir John Cass Technical Institute, which is specially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, September 22nd. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction, which form a special feature of the work of the Institute. In connection with the latter, several new departures are being made for the coming Session. The curriculum in connection with the Fermentation Industries has been much developed, and now includes courses of instruction on Brewing and Malting, Bottling and Cellar Management, Brewery Plant, and on the Micro-biology of the Fermentation Industries. A connected series of lectures dealing with the Supply and Control of Power has also been arranged to meet the requirements of those engaged in works connected with Chemical, Electrical, and the Fermentation Industries. These will comprise a course of 20 lectures on the Supply and Control of Liquid, Gaseous, and Solid Fuel, a course of 5 lectures on Electrical Supply and Control, and a connected course of 5 lectures on the Transmission of Power. In the department of Physics and Mathematics, a special course of Lectures and Demonstrations will be given on Colloids, which will deal with the methods employed in their investigation and their relation to technical problems; also special courses of Lectures on the Methods of Differential and Integral Calculus, and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application and modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses of instruction in general Metallurgy, special courses of an advanced character are provided on Gold, Silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Metals used in the Motor Car Industry, on Mining, Mine Surveying, and on Mineralogy.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Biology, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

East Ham Technical College.—Principal, W. H. Barker, B.Sc. Head of Chemical Department—A. E. Dunstan, D.Sc. (Lond.). Lecturers—F. B. Thole, B.Sc.; E. D. Griffiths, B.Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaice; A. G. Mussell. Chemical Engineering and Gas Engineering—A. J. Nice. Gas Supply—G. Jenkins. Soap Manufacture, and Oils, Fats, and Waxes—A. J. Harvey. Tar Distillation, &c.—A. J. Nice, and A. E. Dunstan, D.Sc. Metallurgy—F. B. Thole, B.Sc. Sugar Manufacture—A. Wade. Evening Classes and Secondary School.

Blackburn Municipal Technical School.—Chemistry: Robert H. Pickard, D.Sc.(Lond.)., &c., assisted by Jos. Yates, M.Sc., F.I.C., Jos. Kenyon, B.Sc., F.I.C., and W. Lewcock, B.Sc. Session opened Monday, Sept. 22. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

Redruth School of Mines (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

Municipal School of Technology, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

Wolverhampton Municipal Science and Technical School.—Principal, J D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D.; Physics, A. T. Harrison, B.Sc.; Botany, Sidney Phillips, Ph.C. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Monday, Sept. 15th. For other particulars and programme, apply G. F. Chell, Secretary.

Municipal Technical Institute, Belfast.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph.D., D.Sc., and Assistants. Day and Evening Courses. Session opened Sept. 1st.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

New Process for the Vulcanisation of Rubber.

In trying to apply practically the fine studies of M. Victor Henri (Assistant in Dr. Dastre's Laboratory of Physiology in the Sorbonne) on the depolymerising action of ultra-violet rays on indiarubber, M. G. Bornstein has just made a curious discovery—*these radiations can vulcanise rubber.*

It is known that, industrially, amongst other ingredients sulphur is mixed with pure rubber by a final heating in an autoclave. This sulphur is combined with the rubber, which is henceforth rendered capable of thoroughly resisting the variations of temperature. Now, in preparing very thin fine pellicles with virgin rubber and a little sulphur, in order to obtain the fixation of the sulphur, that is to say, the vulcanisation, it suffices to enlighten the mixture with ultra-violet radiations.

It remains to be seen if the fact will have any consequence applicable to industry. The fact is, it does not appear that the new method can be substituted for the classical process of vulcanisation; but it would be rash to come to a too decided conclusion; and even if it remains in the theoretical domain, the fact is nevertheless interesting.

Interplanetary Voyages.

M. Esnault Pelteric, the well-known constructor of aeroplanes, has just made a whole series of calculations in order to solve the problem of interplanetary voyages. Actually it appears difficult that flying-machines will exceed a speed of more than 200 kilometres an hour. It would thus take 200 hours, or a little more than eight days, to go round the world. To escape from the attraction of the earth M. Esnault Pelteric has calculated that it would be necessary to endow the projectile that was to leave the earth with a speed of 11 kilometres per second.

The new interplanetary apparatus would no longer seem to be the aeroplane, but a cannon ball, similar to that which Jules Verne imagined in his famous novel "From the Earth to the Moon." This shell would be propelled by rockets having the property of uninterrupted continuity. At a speed of 11 kilometres per second a machine of this kind would go round the world in sixty-six minutes, and from Paris to Nice in less than two minutes. This prodigious speed could be obtained by the disintegration of some kilogrms. of radium. One of these projectiles provided with 27 kilogrms. of radium could make the voyage from the earth to the moon in less than forty-nine hours. It is true that the radium would have to give out all the formidable energy it contains in forty-nine hours, whereas in the actual state of science it would require 2800 years to arrive at the same result. With 400 kilogrms. of radium on board it would be possible to go as far as the planet Venus. But all these calculations are but the sport of statisticians.

An Explanation of certain Earthquakes.

M. Barrois has just read at the Academy of Medicine a memoir of Dr. de Montessus de Ballore on a cause that may be assigned for certain earthquakes. The earthquake that took place on August 9th, 1912, in the neighbourhood of Galipoli in Turkey, was studied on the spot by M. Macovei, who has specially described the geology of the lengthened epicentral region parallel to the sea of Marmora, between Rodosto and Gallipoli. Along the length of 20 kilometres of this axis there exists an overlapping of the Sarmatian on to the Miocene strata. In may then be inferred that a tertonic line of this importance must have a relation of cause to effect with the earthquake.

The Risks of Photographers.

The professional risks of photographers are many, and sometimes very serious. They sometimes affect their cutaneous covering, their blood, and their viscera. The first kind of affection has been known for a long time. In perpetual contact with liquids of variable chemical composition the skin of their hands is exposed to eruptions of various intensity, but generally of an eczematous nature. This, after all, is not special only to photographers. The disorders of the blood, too special in their essence for us to enter into all their details, would, according to M. Agasse Lafont, have two distinct causes; on the one hand, there would be a chronic intoxication caused by the salts of silver, the consequences of which recal those brought on by mercurial poisoning; on the other hand, with perforators of cinematographic films that are a little on the margin of the photographic industry, what is specially to be rendered responsible are the vapours of acetate, of amylic acid, and of acetone, which appear to cause globular lesions resembling those caused by intoxication by benzene. Lastly, M. Thiry, after analysing a work of Lenenberger, who establishes the frequency of malignant tumours in the manufacture of aniline colours, shows that the guilty in this matter might certainly be certain groups of chemical substances to which belong paramidophenol and metol. Consequently there is a possible danger of the same nature for photographers who frequently use chemical bodies of this kind. Although this conclusion may appear pessimist and hasty, it is well to follow the counsel of M. Thiry, who considers that the preservation from these accidents lies in a particularly strict regard to hygiene in photographic work. Special garments for the workshop, careful and frequent washing of hands, ventilation and cleanliness of the workshops and photographic studios, as well as the respiratory mask, useful in certain fabrications, all of which precautions will appear but slightly troublesome when compared with the serious complaints and troubles whose arrival may be thus prevented.

The F-rays do not Exist.

The discovery that was announced of a new series of rays, the F-rays, has just been contradicted. According to very precise and detailed information published by the *Eclair*, it appears that the results obtained are not at all conclusive. The F-rays appear to be an illusion similar to that of which the scientific world was a victim when the physicist Blondlot, Professor at the Faculty of Nancy, professed to have discovered the N rays.

NOTICES OF BOOKS.

Preliminary Chemistry. By H. W. Bausor, M.A. London: University Tutorial Press, Ltd. 1913.

This book contains a short course of practical and theoretical chemistry which covers the syllabus of the Cambridge Preliminary Local Examination. Easy experiments on the nature and composition of air, water, chalk, and salt, and on the properties and simpler compounds of sulphur and carbon are described in such a way that the student should usually be able to perform them with very little help or supervision from the teacher, and the author endeavours by the text to give the student definite knowledge of the facts and principles of chemistry, as well as to train his powers of observation and inference. Each chapter is well summarised, and questions and additional practical exercises are given.

Literatur-Register der Organischen Chemie. ("Register of the Literature of Organic Chemistry"). Edited by R. Stelzner. Vol. I. *The Literature of the Years 1910 and 1911.* Braunschweig: Friedrich Vieweg und Sohn. 1913. (M. 84).

This admirable dictionary of organic compounds follows Richter's system of tabulation, and will be found indispensable by all who are interested in organic research. The compounds of carbon are arranged in order of increasing complexity, and under each empirical formula

references are given to the literature relating to all the compounds having that formula. 22,000 different substances are included in this volume, which covers the years 1910 and 1911. In addition to the references to the literature of each substance, very brief notes are given as to the contents of the papers, &c., quoted, so that some account of the occurrence, properties, and transformations of every substance is to be found in the book.

MISCELLANEOUS.

Tests for Coal-tar Colours in Aniline Lakes.—Messrs. Charles Griffin and Co. have in their list an important and valuable work bearing this title, by George Zerr, translated by Dr. C. Mayer, of Burgdorf. The complex nature of synthetical dyes renders their analysis no easy matter, and the present work should prove exceedingly helpful to workers in this field. Until the advent of this work there was practically no literature on the subject. This volume provides all that is needed, and should be in every laboratory dealing with coal-tar colours.

The Chemical Laboratory Fresenius at Wiesbaden, Germany.—During the Summer Term, 1913, the Chemical Laboratory Fresenius was attended by thirty-six students, including three ladies. Of these twenty-one were from Germany, six from Russia, two from Luxemburg, one from Austria, one from Denmark, one from England, one from France, one from Holland, one from Sweden, and one from Brazil. The Directors of the Institute, Geh. Regierungsrat Prof. Dr. H. Fresenius and Prof. Dr. W. Fresenius, are assisted by four duly qualified lecturers and heads of departments. Besides these there is a staff of thirty-two assistant chemists, including six ladies. The next Winter Term will commence on October 15th. During the Summer Term, 1913, a number of scientific treatises originated from the Laboratory Fresenius; they were published in different chemical journals. As special prints appeared: — "Chemische und physikalisch-chemische Untersuchung der Solquelle zu Liesborn bei Lippstadt i.W., sowie Untersuchung derselben auf Radioaktivität von. Geh. Regierungsrat Prof. Dr. H. Fresenius; Wiesbaden, C. W. Kreidel's Verlag, 1913." "Chemische Untersuchung der Herzogsquelle (Slavonski Evian) zu Orahovica in Slavonien von Geh. Regierungsrat Prof. Dr. H. Fresenius; Wiesbaden, C. W. Kreidel's Verlag, 1913." "Chemische und physikalisch-chemische Untersuchung des Luitpoldsprudels zu Bad Kissingen nebst Untersuchungen über dessen Radioaktivität von Dr. R. Fresenius and Dr. L. Grünhut; Wiesbaden, C. W. Kreidel's Verlag, 1913." Besides the scientific work a great number of chemical analyses were executed during the summer half year, 1913, for commercial, mining, industrial, and agricultural purposes, also in the interest of Sanitary-boards, Criminal and other State Departments.

The Apprenticeship and Skilled Employment Association notifies that it can recommend for work in commercial and other laboratories several promising lads who have been acting as laboratory monitors or assistants in London County Council Higher Grade or Secondary Schools, and whose services the Council are unable to retain after they have reached the age of 17. The Association has already placed some lads in suitable occupations in which they are doing well, and has now had a fresh batch referred to it. Further information may be obtained from the Association, the offices of which are 61, Denison House, Vauxhall Bridge Road, S.W.

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THE CHEMICAL NEWS.

Vol. CVIII., No. 2807.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Birmingham, 1913.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Oliver Lodge, D.Sc., LL.D., F.R.S., &c.

CONTINUITY.

Natura non vincitur nisi parendo.

First let me lament the catastrophe which has led to my occupying the Chair here in this City. Sir William White was a personal friend of many here present, and I would that the citizens of Birmingham could have become acquainted with his attractive personality, and heard at first hand of the strenuous work which he accomplished in carrying out the behests of the Empire in the construction of its first line of defence.

Although a British Association Address is hardly an annual stocktaking, it would be improper to begin this year of Office without referring to three more of our losses:—One that cultured gentleman, amateur of science in the best sense, who was chosen to preside over our Jubilee meeting at York thirty-two years ago. Sir John Lubbock, first Baron Avebury, cultivated science in a spirit of pure enjoyment, treating it almost as one of the Arts; and he devoted social and political energy to the welfare of the multitude of his fellows less fortunately situated than himself.

Through the untimely death of Sir George Darwin the world has lost a mathematical astronomer whose work on the Tides and allied phenomena is a monument of power and achievement. So recently as our visit to South Africa he occupied the Presidential Chair.

By the third of our major losses, I mean the death of that brilliant mathematician of a neighbouring nation who took so comprehensive and philosophic a grasp of the intricacies of physics, and whose eloquent though sceptical exposition of our laws and processes, and of the modifications entailed in them by recent advances, will be sure to attract still more widespread attention among all to whom the rather abstruse subject-matter is sufficiently familiar. I cannot say that I find myself in agreement with all that Henri Poincaré wrote or spoke in the domain of physics, but no physicist can help being interested in his mode of presentation, and I may have occasion to refer, in passing, to some of the topics with which he dealt.

And now, eliminating from our purview, as is always necessary, a great mass of human activity, and limiting ourselves to a scrutiny on the side of pure science alone, let us ask what, in the main, is the characteristic of the promising though perturbing period in which we live. Different persons would give different answers, but the answer I venture to give is—Rapid progress, combined with Fundamental scepticism.

Rapid progress was not characteristic of the latter half of the nineteenth century—at least not in physics. Fine solid dynamical foundations were aid, and the edifice of knowledge was consolidated; but wholly fresh ground was not being opened up, and totally new buildings were not expected.

> "In many cases the student was led o believe that the main facts of nature were all known, that the chances of any great discovery being made by experiment were vanishingly small, and that therefore the experimentalist's work consisted in deciding between rival theories, or in finding some small residual effect, which might add a more or less important detail to the theory."—*Schuster.*

With the realisation of predicted ether waves in 1888, the discovery of X-rays in 1895, spontaneous radio-activity in 1896, and the isolation of the electron in 1898, expectation of further achievement became vivid; and novelties, experimental, theoretical, and speculative, have been showered upon us ever since this century began. That is why I speak of rapid progress.

Of the progress I shall say little—there must always be some uncertainty as to which particular achievement permanently contributes to it; but I will speak about the fundamental scepticism.

Let me hasten to explain that I do not mean the well-worn and almost antique theme of Theological scepticism; that controversy is practically in abeyance just now. At any rate the major conflict is suspended; the forts behind which the enemy has retreated do not invite attack; the territory now occupied by him is little more than his legitimate province. It is the scientific allies, now, who are waging a more or less invigorating conflict among themselves; with philosophers joining in. Meanwhile the ancient foe is biding his time and hoping that from the struggle something will emerge of benefit to himself. Some positions, he feels, were too hastily abandoned and may perhaps be retrieved; or, to put it without metaphor, it seems possible that a few of the things prematurely denied, because asserted on inconclusive evidence, may after all, in some form or other, have really happened. Thus the old theological bitterness is mitigated, and a temporising policy is either advocated or instinctively adopted.

To illustrate the nature of the fundamental scientific or philosophic controversies to which I do refer, would require almost as many addresses as there are Sections of the British Association, or at any rate as many as there are chief cities in Australia; and perhaps my successor in the Chair will continue the theme; but, to exhibit my meaning very briefly, I may cite the kind of dominating controversies now extant, employing as far as possible only a single word in each case so as to emphasise the necessary brevity and insufficiency of the reference.

In Physiology the conflict ranges round *Vitalism*. (My immediate predecessor dealt with the subject at Dundee).

In Chemistry the debate concerns *Atomic structure*. (My penultimate predecessor is well aware of pugnacity in that region).

In Biology the dispute is on the laws of *Inheritance*. (My successor is sure to deal with this subject; probably in a way not deficient in liveliness).

And besides these major controversies, debate is active in other sections.

In Education, *Curricula* generally are being overhauled or fundamentally criticised, and revolutionary ideas are promulgated concerning the advantages of freedom for infants.

In Economic and Political Science, or Sociology, what is there that is not under discussion? Not property alone, nor land alone, but everything—back to the garden of Eden and the inter-relations of men and women.

Lastly, in the vast group of Mathematical and Physical Sciences, "slurred over rather than summed up as Section A," present-day scepticism concerns what, if I had to express it in one word, I should call *Continuity*. The full meaning of this term will hardly be intelligible without explanation, and I shall discuss it presently.

Still more fundamental and deep-rooted than any of these sectional debates, however, a critical examination of scientific foundations generally is going on; and a kind

of philosophic scepticism is in the ascendant, resulting in a mistrust of purely intellectual processes and in a recognition of the limited scope of science.

For science is undoubtedly an affair of the intellect, it examines everything in the cold light of reason; and that is its strength. It is a commonplace to say that science must have no likes or dislikes, must aim only at truth; or as Bertrand Russell well puts it: —

> "The kernel of the scientific outlook is the refusal to regard our own desires, tastes, and interests as affording a key to the understanding of the world."

This exclusive single-eyed attitude of science is its strength; but, if pressed beyond the positive region of usefulness into a field of dogmatic negation and philosophising, it becomes also its weakness. For the nature of man is a large thing, and intellect is only a part of it; a recent part too, which therefore necessarily, though not consciously, suffers from some of the defects of newness and crudity, and should refrain from imagining itself the whole—perhaps it is not even the best part—of human nature.

The fact is that some of the best things are, by abstraction, excluded from Science, though not from Literature and Poetry; hence perhaps an ancient mistrust or dislike of science, typified by the Promethean legend. Science is systematised and *metrical* knowledge, and in regions where measurement cannot be applied it has small scope; or, as Mr. Balfour said the other day at the opening of a new wing of the National Physical Laboratory—

> "Science depends on measurement, and things not measurable are therefore excluded, or tend to be excluded, from its attention. But Life and Beauty and Happiness are not measurable." And then characteristically he adds:—"If there could be a unit of happiness, Politics might begin to be scientific."

Emotion and Intuition and Instinct are immensely older than science, and in a comprehensive survey of existence they cannot be ignored. Scientific men may rightly neglect them, in order to do their proper work, but philosophers cannot.

So Philosophers have begun to question some of the larger generalisations of science, and to ask whether in the effort to be universal and comprehensive we have not extended our laboratory inductions too far. The Conservation of Energy, for instance—is it always and everywhere valid; or may it under some conditions be disobeyed? It would seem as if the second law of Thermodynamics must be somewhere disobeyed—at least if the age of the Universe is both ways infinite—else the final consummation would have already arrived.

Not by philosophers only, but by scientific men also, ancient postulates are being pulled up by the roots. Physicists and Mathematicians are beginning to consider whether the long known and well-established laws of mechanics hold true everywhere and always, or whether the Newtonian scheme must be replaced by something more modern, something to which Newton's laws of motion are but an approximation.

Indeed a whole system of non-Newtonian Mechanics has been devised, having as its foundation the recently discovered changes which must occur in bodies moving at speeds nearly comparable with that of light. It turns out in fact that both Shape and Mass are functions of Velocity. As the speed increases the mass increases and the shape is distorted, though under ordinary conditions only to an infinitesimal extent.

So far I agree; I agree with the statement of fact; but I do not consider it so revolutionary as to overturn Newtonian mechanics. After all, a variation of Mass is familiar enough, and it would be a great mistake to say that Newton's second law breaks down merely because Mass is not constant. A raindrop is an example of variable mass; or the earth may be, by reason of meteoric dust; or the sun, by reason of radio-activity; or a locomotive, by reason of the emission of steam. In fact, variable masses are the commonest, for friction may abrade any moving body to a microscopic extent.

That Mass is constant is only an approximation. That Mass is equal to ratio of Force and Acceleration is a definition, and can be absolutely accurate. It holds perfectly even for an electron with a speed near that of light; and it is by means of Newton's second law that the variation of Mass with Velocity has been experimentally observed and compared with theory.

I urge that we remain with, or go back to, Newton. I see no reason against retaining all Newton's laws, discarding nothing; but supplementing them in the light of further knowledge.

Even the laws of Geometry have been overhauled, and Euclidean Geometry is seen to be but a special case of more fundamental generalisations. How far they apply to existing space, and how far Time is a reality or an illusion, and whether it can in any sense depend on the motion or the position of an observer; all these things in some form or other are discussed.

The Conservation of Matter also, that main-mast of nineteenth century chemistry, and the existence of the Ether of Space, that sheet-anchor of nineteenth century physics,—do they not sometimes seem to be going by the board?

Prof. Schuster, in his American lectures, commented on the modern receptive attitude as follows:—

> "The state of plasticity and flux—a healthy state, in my opinion,—in which scientific thought of the present day adapts itself to almost any novelty, is illustrated by the complacency with which the most cherished tenets of our fathers are being abandoned. Though it was never an article of orthodox faith that chemical elements were immutable and would not some day be resolved into simpler constituents, yet the conservation of mass seemed to lie at the very foundation of the creation. But nowadays the student finds little to disturb him, perhaps too little, in the idea that mass changes with velocity, and he does not always realise the full meaning of the consequences which are involved."

This readiness to accept and incorporate new facts into the scheme of physics may have led to perhaps an undue amount of scientific scepticism, in order to right the balance.

But a still deeper variety of comprehensive scepticism exists, and it is argued that all our laws of nature, so laboriously ascertained and carefully formulated, are but conventions after all, not truths; that we have no faculty for ascertaining real truth, that our intelligence was not evolved for any such academic purpose; that all we can do is to express things in a form convenient for present purposes, and employ that mode of expression as a tentative and pragmatically useful explanation.

Even *explanation*, however, has been discarded as too ambitious by some men of science, who claim only the power to describe. They not only emphasise the *how* rather than the *why*,—as is in some sort inevitable, since explanations are never ultimate—but are satisfied with very abstract propositions, and regard mathematical equations as preferable to, because safer than, mechanical analogies or models.

> "To use an acute and familiar expression of Gustav Kirchhoff, it is the object of science to *describe* natural phenomena, not to *explain* them. When we have expressed by an equation the correct relationship between different natural phenomena we have gone as far as we safely can, and if we go beyond we are entering on purely speculative ground."

But the modes of statement preferred by those who distrust our power of going correctly into detail are far from satisfactory. Professor Schuster describes and comments on them, thus:—

"Vagueness, which used to be recognised as our great enemy, is now being enshrined as an idol to be worshipped. We may never know what constitutes atoms, or what is the real structure of the ether; why trouble therefore, it is said, to find out more about them. Is it not safer, on the contrary, to confine ourselves to a general talk on entropy, luminiferous vectors, and undefined symbols expressing vaguely certain physical relationships? What really lies at the bottom of the great fascination which these new doctrines exert on the present generation is sheer cowardice, the fear of having its errors brought home to it." . . .

"I believe this doctrine to be fatal to a healthy development of science. Granting the impossibility of penetrating beyond the most superficial layers of observed phenomena, I would put the distinction between the two attitudes of mind in this way: One glorifies our ignorance, while the other accepts it as a regrettable necessity."

In further illustration of the modern sceptical attitude, I quote from Poincaré :—

"Principles are conventions and definitions in disguise. They are, however, deduced from experimental laws, and these laws have, so to speak, been erected into principles to which our mind attributes an absolute value." . . .

"The fundamental propositions of geometry, for instance Euclid's postulate, are only conventions, and it is quite as unreasonable to ask if they are true or false as to ask if the metric system is true or false. Only these conventions are convenient." . . .

"Whether the ether exists or not matters little,—let us leave that to the metaphysicians; what is essential for us is that everything happens as if it existed, and that this hypothesis is found to be suitable for the explanation of phenomena. After all, have we any other reason for believing in the existence of material objects? That, too, is only a convenient hypothesis."

As an antidote against over-pressing these utterances I quote from Sir J. Larmor's Preface :—

"There has been of late a growing trend of opinion, prompted in part by general philosophical views, in the direction that the theoretical constructions of physical science are largely factitious, that instead of presenting a valid image of the relations of things on which further progress can be based, they are still little better than a mirage." . . .

"The best method of abating this scepticism is to become acquainted with the real scope and modes of application of conceptions which, in the popular language of superficial exposition—and even in the unguarded and playful paradox of their authors, intended only for the instructed eye—often look bizarre enough."

One thing is very notable, that it is closer and more exact knowledge that has led to the kind of scientific scepticism now referred to; and that the simple laws on which we used to be working were thus simple and discoverable because the full complexity of existence was tempered to our ken by the roughness of our means of observation.

Kepler's laws are not accurately true, and if he had had before him all the data now available he could hardly have discovered them. A planet does not really move in an ellipse but in a kind of hypocycloid, and not accurately in that either.

So it is also with Boyle's law, and the other simple laws in Physical Chemistry. Even Van der Waals' generalisation of Boyle's law is only a further approximation.

In most parts of physics simplicity has sooner or later to give place to complexity: though certainly I urge that the simple laws were true, and are still true, as far as they go, their inaccuracy being only detected by further real discovery. The reason they are departed from becomes known to us; the law is not really disobeyed, but is modified through the action of a known additional cause. Hence it is all in the direction of progress.

It is only fair to quote Poincaré again, now that I am able in the main to agree with him—

"Take, for instance, the laws of reflection. Fresnel established them by a simple and attractive theory which experiment seemed to confirm. Subsequently, more accurate researches have shown that this verification was but approximate; traces of elliptic polarisation were detected everywhere. But it is owing to the first approximation that the cause of these anomalies was found, in the existence of a transition layer; and all the essentials of Fresnel's theory have remained. We cannot help reflecting that all these relations would never have been noted if there had been doubt in the first place as to the complexity of the objects they connect. Long ago it was said: If Tycho had had instruments ten times as precise, we would never have had a Kepler, or a Newton, or Astronomy. It is a misfortune for a science to be born too late, when the means of observation have become too perfect. That is what is happening at this moment with respect to physical chemistry; the founders are hampered in their general grasp by third and fourth decimal places; happily they are men of robust faith. As we get to know the properties of matter better we see that continuity reigns. . . . . It would be difficult to justify [the belief in continuity] by apodeictic reasoning, but without [it] all science would be impossible."

Here he touches on my own theme, *Continuity*; for, if we had to summarise the main trend of physical controversy at present, I feel inclined to urge that it largely turns on the question as to which way ultimate victory lies in the fight between Continuity and Discontinuity.

On the surface of nature at first we see discontinuity; objects detached and countable. Then we realise the air and other media, and so emphasise continuity and flowing quantities. Then we detect atoms and numerical properties, and discontinuity once more makes its appearance. Then we invent the ether and are impressed with continuity again. But this is not likely to be the end; and what the ultimate end will be, or whether there is an ultimate end, is a question difficult to answer.

The modern tendency is to emphasise the discontinuous or atomic character of everything. Matter has long been atomic, in the same sense as Anthropology is atomic; the unit of matter is the atom, as the unit of humanity is the individual. Whether men or women or children—they can be counted as so many "souls." And atoms of matter can be counted too.

Certainly however there is an illusion of continuity. We recognise it in the case of water. It appears to be a continuous medium, and yet it is certainly molecular. It is made continuous again, in a sense, by the ether postulated in its pores; for the ether is essentially continuous. Though Osborne Reynolds, it is true, invented a discontinuous or granular Ether, on the analogy of the sea shore. The sands of the sea, the hairs of the head, the descendants of a Patriarch, are typical instances of numerable, or rather of innumerable, things. The difficulty of enumerating them is not that there is nothing to count, but merely that the things to be counted are very numerous. So are the atoms in a drop of water,—they outnumber the drops in an Atlantic Ocean—and, during the briefest time of stating their number, fifty millions or so may have evaporated; but they are as easy to count as the grains of sand on a shore.

The process of counting is evidently a process applicable to discontinuities, *i.e.*, to things with natural units; you can count apples and coins, and days and years, and people and atoms. To apply number to a continuum you

must first cut it up into artificial units; and you are always left with incommensurable fractions. Thus only is it that you can deal numerically with such continuous phenomena as the warmth of a room, the speed of a bird, the pull of a rope, or the strength of a current.

But how, it may be asked, does discontinuity apply to number? The natural numbers, 1, 2, 3, etc., are discontinuous enough, but there are fractions to fill up the interstices; how do we know that they are not really connected by these fractions, and so made continuous again?

(By number I always mean commensurable number; incommensurables are not numbers: they are just what cannot be expressed in numbers. The square root of 2 is not a number, though it can be readily indicated by a length. Incommensurables are usual in physics and are frequent in geometry; the conceptions of geometry are essentially continuous. It is clear, as Poincaré says, that "if the points whose co-ordinates are commensurable were alone regarded as real, the in-circle of a square and the diagonal of the square would not intersect, since the co-ordinates of the points of intersection are incommensurable.")

I want to explain how commensurable fractions do not connect up numbers, nor remove their discontinuity in the least. The divisions on a foot rule, divided as closely as you please, represent commensurable fractions, but they represent none of the length. No matter how numerous they are, all the length lies between them; the divisions are mere partitions and have consumed none of it; nor do they connect up with each other, they are esentially discontinuous. The interspaces are infinitely more extensive than the barriers which partition them off from one another; they are like a row of compartments with infinitely thin walls. All the incommensurables lie in the interspaces; the compartments are full of them, and they are thus infinitely more numerous than the numerically expressible magnitudes. Take any point of the scale at random, that point will certainly lie in an interspace: it will not lie on a division, for the chances are infinity to 1 against it.

Accordingly incommensurable quantities are the rule in physics. Decimals do not in practice terminate or circulate, in other words vulgar fractions do not accidentally occur in any measurements, for this would mean infinite accuracy. We proceed to as many places of decimals as correspond to the order of accuracy aimed at.

Whenever, then, a commensurable number is really associated with any natural phenomenon, there is necessarily a noteworthy circumstance involved in the fact, and it means something quite definite and ultimately ascertainable. Every discontinuity that can be detected and counted is an addition to knowledge. It not only means the discovery of natural units instead of being dependent on artificial ones, but it throws light also on the nature of phenomena themseives.

For instance:—

The ratio between the velocity of light and the inverted square root of the product of the electric and magnetic constants was discovered by Clerk Maxwell to be 1; and a new volume of physics was by that discovery opened.

Dalton found that chemical combination occurred between quantities of different substances specified by certain whole or fractional numbers; and the atomic theory of matter sprang into substantial though at first infantile existence.

The hypothesis of Prout, which in some modified form seems likely to be substantiated, is that all atomic weights are commensurable numbers; in which case there must be a natural fundamental unit underlying, and in definite groups composing, the atoms of every form of matter.

The small number of degrees of freedom of a molecule, and the subdivision of its total energy into equal parts corresponding thereto, is a theme not indeed without difficulty but full of importance. It is responsible for the suggestion that energy too may be atomic!

Mendeleeff's series again, or the detection of a natural grouping of atomic weights in families of seven, is another example of the significance of number.

Electricity was found by Faraday to be numerically connected with quantity of matter; and the atom of electricity began its hesitating but now brilliant career.

Electricity itself—*i.e.*, electric charge—strangely enough has proved itself to be atomic. There is a natural unit of electric charge, as suspected by Faraday and Maxwell and named by Johnstone Stoney. Some of the electron's visible effects were studied by Crookes in a vacuum; and its weighing and measuring by J. J. Thomson were announced to the British Association Meeting at Dover in 1899,—a fitting prelude to the twentieth century.

An electron is the natural unit of negative electricity, and it may not be long before the natural unit of positive electricity is found too. But concerning the nature of the positive unit there is at present some division into opposite camps. One school prefers to regard the unit of positive electricity as a homogeneous sphere, the size of an atom, in which electrons revolve in simple harmonic orbits and constitute nearly the whole effective mass. Another school, while appreciative of the simplicity and ingenuity and beauty of the details of this conception, and the skill with which it has been worked out, yet thinks the evidence more in favour of a minute central positive nucleus, or nucleus-group, of practically atomic mass; with electrons, larger—*i.e.*, less concentrated—and therefore less massive than itself, revolving round it in astronomical orbits. While from yet another point of view it is insisted that positive and negative electrons can only differ skew-symmetrically, one being like the image of the other in a mirror, and that the mode in which they are grouped to form an atom remains for future discovery. But no one doubts that electricity is ultimately atomic.

Even magnetism has been suspected of being atomic, and its hypothetical unit has been named in advance the magneton: but I confess that here I have not been shaken out of the conservative view.

We may express all this as an invasion of number into unsuspected regions.

Biology may be said to be becoming atomic. It has long had natural units in the shape of cells and nuclei, and some discontinuity represented by body-boundaries and cell-walls; but now, in its laws of heredity as studied by Mendel, number and discontinuity are strikingly apparent among the reproductive cells, and the varieties of offspring admit of numerical specification and prediction to a surprising extent; while modification by continuous variation, which seemed to be of the essence of Darwinism, gives place to, or at least is accompanied by, mutation, with finite and considerable and in appearance discontinuous change.

So far from Nature not making jumps, it becomes doubtful if she does anything else. Her hitherto placid course, more closely examined, seems to look like a kind of steeplechase.

Yet undoubtedly Continuity is the backbone of evolution, as taught by all biologists,—no artificial boundaries or demarcations between species—a continuous chain of heredity from far below the amœba up to man. Actual continuity of undying germ-plasm, running through all generations, is taught likewise; though a strange discontinuity between this persistent element and its successive accessory body-plasms—a discontinuity which would convert individual organisms into mere temporary accretions or excretions, with no power of influencing or conveying experience to their generating cells—is advocated by one school.

Discontinuity does not fail to exercise fascination even in pure Mathematics. Curves are invented which have no tangent or differential coefficient, curves which consist of a succession of dots or of twists; and the theory of commensurable numbers seems to be exerting a dominance over philosophic mathematical thought as well as over physical problems.

And not only these fairly accepted results are prominent, but some more difficult and unexpected theses in the same direction are being propounded, and the atomic character of Energy is advocated. We had hoped to be honoured by the presence of Professor Planck, whose theory of the *quantum*, or indivisible unit or atom of energy, excites the greatest interest, and by some is thought to hold the field.

Then, again, Radiation is showing signs of becoming atomic or discontinuous. The corpuscular theory of radiation is by no means so dead as in my youth we thought it was. Some radiation is certainly corpuscular, and even the etherial kind shows indications, which may be misleading, that it is spotty, or locally concentrated into points, as if the wave front consisted of detached specks or patches; or, as J. J. Thomson says, "the wave-front must be more analogous to bright specks on a dark ground than to a uniformly illuminated surface," thus suggesting that the Ether may be fibrous in structure, and that a wave runs along lines of electric force; as the genius of Faraday surmised might be possible, in his "Thoughts on Ray Vibrations." Indeed, Newton guessed something of the same kind, I fancy, when he superposed ether-pulses on his corpuscles.

Whatever be the truth in this matter, a discussion on Radiation, of extreme weight and interest, though likewise of great profundity and technicality, is expected on Friday in Section A. We welcome Prof. Lorentz, Dr. Arrhenius, Prof. Langevin, Prof. Pringsheim, and others, some of whom have been specially invited to England because of the important contributions which they have made to the subject-matter of this discussion.

Why is so much importance attached to Radiation? Because it is the best-known and longest-studied link between matter and ether, and the only property we are acquainted with that affects the unmodified great mass of ether alone. Electricity and magnetism are associated with the modifications or singularities called electrons; most phenomena are connected still more directly with matter. Radiation, however, though excited by an accelerated electron, is subsequently let loose in the ether of space, and travels as a definite thing at a measurable and constant pace—a pace independent of everything so long as the ether is free, unmodified, and unloaded by matter. Hence radiation has much to teach us, and we have much to learn concerning its nature.

How far can the analogy of granular, corpuscular, countable, atomic, or discontinuous things be pressed? There are those who think it can be pressed very far. But to avoid misunderstanding let me state, for what it may be worth, that I myself am an upholder of *ultimate* Continuity, and a fervent believer in the Ether of Space.

We have already learnt something about the ether; and although there may be almost as many varieties of opinion as there are people qualified to form one, in my view we have learnt as follows:—

The Ether is the universal connecting medium which binds the universe together, and makes it a coherent whole instead of a chaotic collection of independent isolated fragments. It is the vehicle of transmission of all manner of force, from gravitation down to cohesion and chemical affinity; it is therefore the storehouse of potential energy.

Matter moves, but Ether is strained.

What we call elasticity of matter is only the result of an alteration of configuration due to movement and readjustment of particles, but all the strain and stress are in the ether. The ether itself does not move, that is to say, it does not move in the sense of locomotion, though it is probably in a violent state of rotational or turbulent motion in its smallest parts; and to that motion its exceeding rigidity is due.

As to its density, it must be far greater that that of any form of matter, millions of times denser than lead or platinum. Yet matter moves through it with perfect freedom, without any friction or viscosity. There is nothing paradoxical in this: viscosity is not a function o density; the two are not necessarily connected. When a solid moves through an alien fluid it is true that it acquires a spurious or apparent extra inertia from the fluid it displaces; but, in the case of matter and ether, not only is even the densest matter excessively porous and discontinuous, with vast interspaces in and among the atoms, but the constitution of matter is such that there appears to be no displacement in the ordinary sense at all; the ether is itself so modified as to *constitute* the matter in some way. Of course that portion moves, its inertia is what we observe, and its amount depends on the potential energy in its associated electric field, but the motion is not like that of a foreign body, it is that of some inherent and merely individualised portion of the stuff itself. Certain it is that the ether exhibits no trace of viscosity.*

Matter in motion, Ether under strain, constitute the fundamental concrete things we have to do with in physics. The first pair represent kinetic energy, the second potential energy; and all the activities of the material universe are represented by alternations from one of these forms to the other.

Whenever this transference and transformation of energy occur, work is done, and some effect is produced, but the energy is never diminished in quantity; it is merely passed on from one body to another, always from ether to matter or vice versa,—except in the case of radiation, which simulates matter—and from one form to another.

The forms of energy can be classified as either a translation, a rotation, or a vibration of pieces of matter of different sizes, from stars and planets down to atoms and electrons; or else an etherial strain which in various different ways is manifested by the behaviour of such masses of matter as appeal to our senses.†

Some of the facts responsible for the suggestion that energy is atomic seem to me to depend on the discontinuous nature of the structure of a material atom, and on the high velocity of its constituent particles. The apparently discontinuous emission of radiation is, I believe, due to features in the real discontinuity of matter. Disturbances inside an atom appear to be essentially catastrophic; a portion is liable to be ejected with violence. There appears to be a critical velocity below which ejection does not take place; and, when it does, there also occurs a sudden re arrangement of parts which is presumably responsible for some perceptible etherial radiation. Hence it is, I suppose, that radiation comes off in gushes or bursts; and hence it appears to consist of indivisible units. The occasional phenomenon of new stars, as compared with the steady orbital motion of the millions of recognised bodies, may be suggested as an astronomical analogue.

The hypothesis of *quanta* was devised to reconcile the law that the energy of a group of colliding molecules must in the long run be equally shared among all their degrees of freedom, with the observed fact that the energy is really shared into only a small number of equal parts. For if vibration-possibilities have to be taken into account, the number of degrees of molecular freedom must be very large, and energy shared among them ought soon to be all frittered away; whereas it is not. Hence the idea is suggested that minor degrees of freedom are initially excluded from sharing the energy, because they cannot be supplied with less than one atom of it.

I should prefer to express the fact by saying that the ordinary encounters of molecules are not of a kind able to excite atomic vibrations, or in any way to disturb the ether. Spectroscopic or luminous vibrations of an atom are excited only by an exceptionally violent kind of collision, which may be spoken of as chemical clash; the ordinary molecular orbital encounters, always going on at the rate

* For details of my experiment on this subject see *Phil. Trans. Roy. Soc.* for 1893 and 1897; or a very abbreviated reference to it, and to the other matters above-mentioned, in my small book "The Ether of Space."

† See, in the *Philosophical Magazine* for 1879, my article on "A Classification of the Forms of Energy."

of millions a second, are ineffective in that respect, except in the case of phosphorescent or luminescent substances. That common molecular deflections *are* ineffective is certain, else all the energy would be dissipated or transferred from matter into the ether; and the reasonableness of their radiative inefficiency is not far to seek, when we consider the comparatively leisurely character of molecular movements, at speeds comparable with the velocity of sound. Admittedly, however, the effective rigidity of molecules must be complete, otherwise the sharing of energy must ultimately occur. They do not seem able to be set vibrating by anything less than a certain minimum stimulus; and that is the basis for the theory of *quanta*.

Quantitative applications of Planck's theory, to elucidate the otherwise shaky stability of the astronomically constituted atom, have been made; and the agreement between results so calculated and those observed, including a determination of series of spectrum lines, is very remarkable. One of the latest contributions to this subject is a paper by Dr. Bohr in the *Philosophical Magazine* for July this year.

To show that I am not exaggerating the modern tendency towards discontinuity, I quote from Poincaré's *Dernières Pensées*, a proposition which he announces in italics as representing a form of Prof. Planck's view of which he apparently approves:—

> "A physical system is susceptible of a finite number only of distinct conditions; it jumps from one of these conditions to another without passing through a continuous series of intermediate conditions."

Also this from Sir Joseph Larmor's Preface to Poincaré's *Science and Hypothesis*:—

> "Still more recently it has been found that the good Bishop Berkeley's logical gibes against the Newtonian ideas of fluxions and limiting ratios cannot be adequately appeased in the rigorous mathematical conscience, until our apparent continuities are resolved mentally into discrete aggregates which we only partially apprehend. The irresistible impulse to atomise everything thus proves to be not merely a disease of the physicist; a deeper origin, in the nature of knowledge itself, is suggested."

One very valid excuse for this prevalent attitude is the astonishing progress that has been made in actually seeing or almost seeing the molecules, and studying their arrangement and distribution.

The laws of gases have been found to apply to emulsions and to fine powders in suspension, of which the Brownian movement has long been known. This movement is caused by the orthodox molecular bombardment, and its average amplitude exactly represents the theoretical mean free path calculated from the "molecular weight" of the relatively gigantic particles. The behaviour of these microscopically visible masses corresponds closely and quantitatively with what could be predicted for them as fearfully heavy atoms, on the kinetic theory of gases; they may indeed be said to constitute a gas with a grm.-molecule as high as 200,000 tons; and, what is rather important as well as interesting, they tend visibly to verify the law of equipartition of energy even in so extreme a case, when that law is properly stated and applied.

Still more remarkable—the application of X-rays to display the arrangement of molecules in crystals, and ultimately the arrangement of atoms in molecules, as initiated by Prof. Laue with Drs. Friedrich and Knipping, and continued by Prof. Bragg and his son and by Dr. Tutton, constitute a series of researches of high interest and promise. By this means many of the theoretical anticipations of our countryman, Mr. William Barlow, and—working with him—Prof. Pope, as well as of those distinguished crystallographers von Groth and von Fedorow, have been confirmed in a striking way. These brilliant researches, which seem likely to constitute a branch of Physics in themselves, and which are being continued by Messrs. Moseley and C. G. Darwin, and by Mr. Keene and others, may be called an apotheosis of the atomic theory of matter.

One other controversial topic I shall touch upon in the domain of physics, though I shall touch upon it lightly, for it is not a matter for easy reference as yet. If the *Principle of Relativity* in an extreme sense establishes itself, it seems as if even Time would become discontinuous and be supplied in atoms, as money is doled out in pence or centimes instead of continuously;—in which case our customary existence will turn out to be no more really continuous than the events on a kinematograph screen,—while that great agent of continuity, the Ether of Space, will be relegated to the museum of historical curiosities.

In that case differential equations will cease to represent the facts of nature, they will have to be replaced by Finite Differences, and the most fundamental revolution since Newton will be inaugurated.

Now in all the debateable matters of which I have indicated possibilities I want to urge a conservative attitude. I accept the new experimental results on which some of these theories—such as the Principle of Relativity—are based, and am profoundly interested in them, but I do not feel that they are so revolutionary as their propounders think. I see a way to retain the old and yet embrace the new, and I urge moderation in the uprooting and removal of landmarks.

And of these the chief is Continuity. I cannot imagine the exertion of mechanical force across empty space, no matter how minute; a continuous medium seems to me essential. I cannot admit discontinuity in either Space or Time, nor can I imagine any sort of experiment which would justify such a hypothesis. For surely we must realise that we know nothing experimental of either space or time, we cannot modify them in any way. We make experiments on bodies, and only on bodies, using "body" as an exceedingly general term.

We have no reason to postulate anything but continuity for space and time. We cut them up into conventional units for convenience sake, and those units we can count; but there is really nothing atomic or countable about the things themselves. We can count the rotations of the earth, or the revolutions of an electron, or the vibrations of a pendulum, or the waves of light. All these are concrete and tractable physical entities; but space and time are ultimate data, abstractions based on experience. We know them through motion, and through motion only, and motion is essentially continuous. We ought clearly to discriminate between things themselves and our mode of measuring them. Our measures and perceptions may be affected by all manner of incidental and trivial causes, and we may get confused or hampered by our own movement; but there need be no such complication in things themselves, any more than a landscape is distorted by looking at it through an irregular window-pane or from a travelling coach. It is an ancient and discarded fable that complications introduced by the motion of an observer are real complications belonging to the outer universe.

Very well, then, what about the Ether, is that in the same predicament? Is that an abstraction, or a mere convention, or is it a concrete physical entity on which we can experiment?

Now it has to be freely admitted that it is exceedingly difficult to make experiments on the ether. It does not appeal to sense, and we know no means of getting hold of it. The one thing we know metrical about it is the velocity with which it can transmit transverse waves. That is clear and definite, and thereby to my judgment it proves itself a physical agent; not indeed tangible or sensible, but yet concretely real.

But it does elude our laboratory grasp. If we rapidly move matter through it, hoping to grip it and move it too, we fail; there is no mechanical connexion. And even if we experiment on light we fail too. So long as transparent matter is moving relatively to us, light can be affected inside that matter; but when matter is relatively stationary

to matter nothing observable takes place, however fast things may be moving, so long as they move together.

Hence arises the idea that motion with respect to Ether is meaningless: and the fact that only relative motion of pieces of matter with respect to each other has so far been observed is the foundation of the Principle of Relativity. It sounds simple enough as thus stated, but in its developments it is an ingenious and complicated doctrine embodying surprising consequences which have been worked out by Professor Einstein and his disciples with consummate ingenuity.

What have I to urge against it? Well, in the first place, it is only in accordance with common sense that no effect of the first order can be observed without relative motion of matter. An Ether-stream through our laboratories is optically and electrically undetectable, at least as regards first order observation; this is clearly explained for general readers in my book *The Ether of Space*, Chapter IV. But the Principle of Relativity says more than that, it says that no effect of any order of magnitude can ever be observed without the relative motion of matter.

The truth underlying this doctrine is that absolute motion without reference to *anything* is unmeaning. But the narrowing down of "anything" to mean any piece of matter is illegitimate. The nearest approach to absolute motion that we can physically imagine is motion through or with respect to the Ether of Space. It is natural to assume that the Ether is on the whole stationary, and to use it as a standard of rest; in that sense motion with reference to it may be called absolute, but in no other sense.

The Principle of Relativity claims that we can never ascertain such motion: in other words, it practically or pragmatically denies the existence of the Ether. Every one of our scientifically observed motions, it says, are of the same nature as our popularly observed ones, viz., motion of pieces of matter relatively to each other; and that is all that we can ever know. Everything goes on—says the Principle of Relativity—as if the Ether did not exist.

Now the facts are that no motion with reference to the ether alone has ever yet been observed: there are always curious compensating effects which just cancel out the movement-terms and destroy or effectively mask any phenomenon that might otherwise be expected. When matter moves past matter observation can be made; but, even so, no consequent locomotion of ether, outside the actually moving particles, can be detected.

(It is sometimes urged that rotation is a kind of absolute motion that can be detected, even in isolation. It can so be detected, as Newton pointed out; but in cases of rotation matter on one side the axis is moving in the opposite direction to matter on the other side of the axis; hence rotation involves relative material motion, and therefore can be observed).

To detect motion through ether we must use an etherial process. We may use radiation, and try to compare the speeds of light along or across the motion; or we might try to measure the speed, first with the motion and then against it. But how are we to make the comparison? If the time of emission from a distant source is given by a distant clock, that clock must be observed through a telescope, that is by a beam of light; which is plainly a compensating process. Or the light from a neighbouring source can be sent back to us by a distant mirror; when again there will be compensation. Or the starting of light from a distant terrestrial source may be telegraphed to us, either with a wire or without; but it is the ether that conveys the message in either case, so again there will be compensation. Electricity, Magnetism, and Light, are all effects of the ether.

Use Cohesion, then; have a rod stretching from one place to another, and measure that. But cohesion is transmitted by the ether too, if, as believed, it is the universal binding medium. Compensation is likely; compensation can, on the electrical theory of matter, be predicted.

Use some action not dependent on Ether, then. Very well, where shall we find it?

To illustrate the difficulty I will quote a sentence from Sir Joseph Larmor's paper before the International Congress of Mathematicians at Cambridge last year.

> "If it is correct to say with Maxwell that all radiation is an electrodynamic phenomenon, it is equally correct to say with him that all electrodynamic relations between material bodies are established by the operation on the molecules of those bodies, of fields of force which are propagated in free space as radiation, and in accordance with the laws of radiation, from one body to the other."

The fact is we are living in an epoch of some very comprehensive generalisations. The physical discovery of the twentieth century, so far, is the Electrical Theory of Matter. This is the great new theory of our time; it was referred to, in its philosophical aspect, by Mr. Balfour in his Presidential Address at Cambridge in 1904. We are too near it to be able to contemplate it properly; it has still to establish itself and to develop in detail, but I anticipate that in some form or other it will prove true.*

Here is a briefest possible summary of the first chapter (so to speak) of the Electrical Theory of Matter.

1. Atoms of Matter are composed of electrons,—of positive and negative electric charges.
2. Atoms are bound together into molecules by chemical affinity which is intense electrical attraction at ultra-minute distances.
3. Molecules are held together by cohesion, which I for one regard as residual or differential chemical affinity over molecular distances.
4. Magnetism is due to the locomotion of electrons. There is no magnetism without an electric current, atomic or otherwise. There is no electric current without a moving electron.
5. Radiation is generated by every accelerated electron, in amount proportional to the square of its acceleration; and there is no other kind of radiation, except indeed a corpuscular kind; but this depends on the velocity of electrons, and therefore again can only be generated by their acceleration.

The theory is bound to have curious consequences; and already it has contributed to some of the uprooting and uncertainty that I speak of. For, if it be true, every material interaction will be electrical, *i.e.*, etherial; and hence arises our difficulty. Every kind of force is transmitted by the ether, and hence, so long as all our apparatus is travelling together at one and the same pace, we have no chance of detecting the motion. That is the strength of the Principle of Relativity. The changes are not zero, but they cancel each other out of observation.

Many forms of statement of the famous Michelson-Morley experiment are misleading. It is said to prove that the time taken by light to go with the ether stream is the same as that taken to go against or across it. It does not show that. What it shows is that the time taken by light to travel to and fro on a measured interval fixed on a rigid block of matter is independent of the aspect of that block with respect to any motion of the earth through space. A definite and most interesting result; but it may be, and often is, interpreted loosely and too widely.

It is interpreted too widely, as I think, when Professor Einstein goes on to assume that no non-relative motion of matter can be ever observed even when *light* is brought into consideration. The relation of light to matter is very curious. The wave front of a progressive wave simulates many of the properties of matter. It has energy, it has momentum, it exerts force, it sustains reaction. It has been described as a portion of the mass of a radiating body,—which gives it a curiously and unexpectedly corpuscular "feel." But it has a definite velocity. Its velocity in space relative to the ether is an absolute constant independent of the motion of the source. This would not be true for corpuscular light.

* For a general introductory account of the electrical theory of matter my Romanes Lecture for 1913 (Clarendon Press) may be referred to.

Hence I hold that here is something with which our own motion may theoretically be compared; and I predict that our motion through the ether will some day be detected by help of this very fact,—by comparing our speed with that of light: though the old astronomical aberration, which seemed to make the comparison easy, failed to do so quite simply, because it is complicated by the necessity of observing the position of a distant source, in relation to which the earth is moving. If the source and observer are moving together there is no possibility of observing aberration. Nevertheless, I maintain that when matter is moving near a beam of light we may be able to detect the motion. For the velocity of light in space is no function of the velocity of the source, nor of matter near it; it is quite unaffected by source or receiver. Once launched it travels in its own way. If we are travelling to meet it, it will be arriving at us more quickly; if we travel away from it, it will reach us with some lag. And observation of the acceleration or retardation is made by aid of Jupiter's satellites. We have there the dial of a clock, to or from which we advance or recede periodically. It gains while we approach it, it loses while we recede from it, it keeps right time when we are stationary or only moving across the line of sight.

But then of course it does not matter whether Jupiter is standing still and we are moving, or vice versa; it is a case of relative motion of matter again. So it is if we observe a Doppler effect from the right and left hand limbs of the rotating sun. True, and if we are to permit no relative motion of matter we must use a terrestrial source, clamped to the earth as our receiver is. And now we shall observe nothing.

But not because there is nothing to observe. Lag must really occur if we are running away from the light, even though the source is running after us at the same pace; unless we make the assumption,—true only for corpuscular light,—that the velocity of light is not an absolute thing, but is dependent on the speed of the source. With corpuscular light there is nothing to observe; with wave light there is something, but we cannot observe it.

But if the whole solar system is moving through the ether I see no reason why the relative ether drift should not be observed by a differential residual effect in connection with Jupiter's satellites or the right and left limbs of the sun. The effect must be too small to observe without extreme precision, but theoretically it ought to be there. Inasmuch, however, as relative motion of matter with respect to the observer is involved in these effects it may be held that the detection of a uniform drift of the solar system in this way is not contrary to the Principle of Relativity. It is contrary to some statements of that Principle; and the cogency of those statements breaks down, I think, whenever they include the velocity of light; because there we really have something absolute (in the only sense in which the term can have a physical meaning) with which we can compare our own motions, when we have learnt how.

But in ordinary astronomical translation—translation as of the earth in its orbit—all our instruments, all our standards, the whole contents of our laboratory, are moving at the same rate in the same direction; under those conditions we cannot expect to observe anything. Clerk Maxwell went so far as to say that if every particle of matter simultaneously received a graduated blow so as to produce a given constant acceleration all in the same direction, we should be unaware of the fact. He did not then know all that we know about radiation. But apart from that, and limiting ourselves to comparatively slow changes of velocity, our standards will inevitably share whatever change occurs. So far as observation goes, everything will be practically as if no change had occurred at all; though that may not be the truth. All that experiment establishes is that there have so far always been compensations; so that the attempt to observe motion through the ether is being given up as hopeless.

Surely, however, the minute and curious compensations cannot be accidental, they must be necessary? Yes, they are necessary; and I want to say why. Suppose the case were one of measuring thermal expansion; and suppose everything had the same temperature and the same expansibility; our standards would contract or expand with everything else, and we could observe nothing; but expansion would occur nevertheless. That is obvious, but the following assertion is not so obvious. If everything in the Universe had the same temperature, no matter what that temperature was, nothing would be visible at all; the external world, so far as vision went, would not appear to exist. Visibility depends on radiation, on differential radiation. We must have differences to appeal to our senses, they are not constructed for uniformity.

It is the extreme omnipresence and uniformity and universal agency of the ether of space that makes it so difficult to observe. To observe anything you must have differences. If all actions at a distance are conducted at the same rate through the ether, the travel of none of them can be observed. Find something not conveyed by the ether and there is a chance. But then every physical action is transmitted by the ether, and in every case by means of its transverse or radiation-like activity.

Except perhaps Gravitation. That may give us a clue some day, but at present we have not been able to detect its speed of transmission at all. No plan has been devised for measuring it. Nothing short of the creation or destruction of matter seems likely to serve; creation or destruction of the gravitational unit, whether it be an atom or an electron or whatever it is. Most likely the unit of weight is an electron, just as the unit of mass is.

The so-called non-Newtonian Mechanics, with mass and shape a function of velocity, is an immediate consequence of the electrical theory of matter. The dependence of inertia and shape on speed is a genuine discovery, and, I believe, a physical fact. The Principle of Relativity would reduce it to a conventional fiction. It would seek to replace this real change in matter by imaginary changes in time. But surely we must admit that Space and Time are essentially unchangeable; they are not at the disposal even of mathematicians; though it is true that Pope Gregory, or a Daylight-saving Bill, can play with our units, can turn the 3rd of October in any one year into the 14th, or can make the sun South sometimes at eleven o'clock sometimes at twelve.*

But the changes of dimension and mass due to velocity are not conventions, but realities; so I urge, on the basis of the electrical theory of matter. The Fitzgerald-Lorentz hypothesis I have an affection for. I was present at its birth. Indeed I assisted at its birth; for it was in my study at 21, Waverley Road, Liverpool, with Fitzgerald in an arm chair, and while I was enlarging on the difficulty of reconciling the then new Michelson experiment with the theory of astronomical aberration and with other known facts, that he made his brilliant surmise:—"Perhaps the stone slab was affected by the motion." I rejoined that it was a 45° shear that was needed. To which he replied, "Well, that's all right—a simple distortion." And very soon he said, "And I believe it occurs, and that the Michelson experiment demonstrates it." A shortening long-ways, or a lengthening cross-ways would do what was wanted.

And is such a hypothesis gratuitous? Not at all; in the light of the electrical theory of matter such an effect ought to occur. The amount required by the experiment, and given by the theory, is equivalent to a shrinkage of the earth's diameter by rather less than 3 inches, in the line of its orbital motion through the ether of space. An oblate spheroid with the proper excentricity has all the simple geometrical properties of a stationary sphere; the

* In the historical case of governmental interference with the calendar, no wonder the Populace rebelled. Surely someone might have explained to the authorities that dropping leap year for the greater part of a century would do all that was wanted, and that the horrible inconvenience of upsetting all engagements and shortening a single year by eleven days could be avoided.

excentricity depends in a definite way on speed, and becomes considerable as the velocity of light is approached.

All this Profs. Lorentz and Larmor very soon after, and quite independently, perceived; though this is only one of the minor achievements in the electrical theory of matter which we owe to our distinguished visitor Prof. H. A. Lorentz.

The key of the position, to my mind, is the nature of cohesion. I regard cohesion as residual chemical affinity, a balance of electrical attraction over repulsion between groups of alternately charged molecules. Lateral electrical attraction is diminished by motion; so is lateral electric repulsion. In cohesion both are active, and they nearly balance. At anything but molecular distance they quite balance, but at molecular distance attraction predominates. It is the diminution of the predominant partner that will be felt. Hence, while longitudinal cohesion, or cohesion in the direction of motion, remains unchanged, lateral cohesion is less; so there will be distortion, and a unit cube $x\ y\ z$ moving along x with velocity u becomes a parallelopiped with sides $1/k^2, k, k$; where $1/k^2 = 1 - u^2/v^2$.*

The electrical theory of matter is a positive achievement, and has positive results. By its aid we make experiments which throw light upon the relation between matter and the Ether of Space. The Principle of Relativity, which seeks to replace it, is a principle of negation, a negative proposition, a statement that observation of certain facts can never be made, a denial of any relation between matter and ether, a virtual denial that the ether exists. Whereas if we admit the real changes that go on by reason of rapid motion, a whole field is open for discovery; it is even possible to investigate the changes in shape of an electron—appallingly minute though it is—as it approaches the speed of light; and properties belonging to the Ether of Space, evasive though it be, cannot lag far behind.

Speaking as a physicist I must claim the Ether as peculiarly our own domain. The study of molecules we share with the chemist, and matter in its various forms is investigated by all men of science, but a study of the ether of space belongs to physics only. I am not alone in feeling the fascination of this portentous entity. Its curiously elusive and intangible character, combined with its universal and unifying permeance, its apparently infinite extent, its definite and perfect properties, make the ether the most interesting as it is by far the largest and most fundamental ingredient in the material cosmos.

As Sir J. J. Thomson said at Winnipeg—

> "The ether is not a fantastic creation of the speculative philosopher; it is as essential to us as the air we breathe. . . . The study of this all-pervading substance is perhaps the most fascinating and important duty of the physicist."

Matter it is not, but material it is; it belongs to the material universe and is to be investigated by ordinary methods. But to say this is by no means to deny that it may have mental and spiritual functions to subserve in some other order of existence, as Matter has in this.

The ether of space is at least the great engine of continuity. It may be much more, for without it there could hardly be a material universe at all. Certainly, however, it is essential to continuity; it is the one all-permeating substance that binds the whole of the particles of matter together. It is the uniting and binding medium without which, if matter could exist at all, it could exist only as chaotic and isolated fragments; and it is the universal medium of communication between worlds and particles. And yet it is possible for people to deny its existence, because it is unrelated to any of our senses, except sight, and to that only in an indirect and not easily recognised fashion.

To illustrate the thorough way in which we may be unable to detect what is around us unless it has some link or bond which enables it to make appeal, let me make another quotation from Sir J. J. Thomson's Address at Winnipeg in 1909. He is leading up to the fact that even single atoms, provided they are fully electrified with the proper atomic charge, can be detected by certain delicate instruments—their field of force bringing them within our ken—whereas a whole crowd of unelectrified ones would escape observation.

> "The smallest quantity of unelectrified matter ever detected is probably that of neon, one of the inert gases of the atmosphere. Prof. Strutt has shown that the amount of neon in 1/20 of a cubic centimetre of the air at ordinary pressures can be detected by the spectroscope. Sir William Ramsay estimates that the neon in the air only amounts to one part of neon in 100,000 parts of air, so that the neon in 1/20 of a cubic centimetre of air would only occupy at atmospheric pressure a volume of half a millionth of a cubic centimetre. When stated in this form the quantity seems exceedingly small, but in this small volume there are about ten million million molecules. Now the population of the earth is estimated at about fifteen hundred millions, so that the smallest number of molecules of neon we can identify is about 7000 times the population of the earth. In other words, if we had no better test for the existence of a man than we have for that of an unelectrified molecule we should come to the conclusion that the earth is uninhabited."

The parable is a striking one, for on these lines it might legitimately be contended that we have no right to say positively that even space is uninhabited. All we can safely say is that we have no means of detecting the existence of non-planetary immaterial dwellers, and that unless they have some link or bond with the material they must always be physically beyond our ken. We may therefore for practical purposes legitimately treat them as non-existent until such link is discovered, but we should not dogmatise about them. True agnosticism is legitimate, but not the dogmatic and positive and gnostic variety.

For I hold that Science is incompetent to make comprehensive denials, even about the Ether, and that it goes wrong when it makes the attempt. Science should not deal in negations; it is strong in affirmations, but nothing based on abstraction ought to presume to deny outside its own region. It often happens that things abstracted from and ignored by one branch of science may be taken into consideration by another:—

Thus, Chemists ignore the Ether.
Mathematicians may ignore experimental difficulties.
Physicists ignore and exclude live things.
Biologists exclude Mind and Design.
Psychologists may ignore human origin and human destiny.
Folk-lore students and comparative Mythologists need not trouble about what modicum of truth there may be in the legends which they are collecting and systematising.
And Microscopists may ignore the stars.

Yet none of these ignored things should he denied.

Denial is no more infallible than assertion. There are cheap and easy kinds of scepticism, just as there are cheap and easy kinds of dogmatism; in fact scepticism can become viciously dogmatic, and science has to be as much on its guard against personal predilection in the negative as in the positive direction. An attitude of universal denial may be very superficial.

> "To doubt everything or to believe everything are two equally convenient solutions; both dispense with the necessity of reflection."

* Different modes of estimating the change give slightly different results; some involve a compression as well as a distortion—in fact, the strain associated with the name of Thomas Young; the details are rather complicated and this is not the place to discuss them. A pure shear, of magnitude specified in the text, is simplest, it is in accord with all the experimental facts—including some careful measurements by Bucherer—and I rather expect it to survive.

All intellectual processes are based on abstraction. For instance, History must ignore a great multitude of facts in order to treat any intelligently: it selects. So does Art; and that is why a drawing is clearer than reality. Science makes a diagram of reality, displaying the works like a skeleton clock. Anatomists dissect out the nervous system, the blood vessels, and the muscles, and depict them separately,—there must be discrimination for intellectual grasp,—but in life they are all merged and co-operating together; they do not really work separately, though they may be studied separately. A scalpel discriminates: a dagger or a bullet crashes through everything. That is life,—or rather death. The laws of nature are a diagrammatic framework, analysed or abstracted out of the full comprehensiveness of reality.

Hence it is that Science has no authority in denials. To deny effectively needs much more comprehensive knowledge than to assert. And abstraction is essentially not comprehensive; one cannot have it both ways. Science employs the methods of abstraction and thereby makes its discoveries.

The reason why some physiologists insist so strenuously on the validity and self-sufficiency of the laws of physics and chemistry, and resist the temptation to appeal to unknown causes—even though the guiding influence and spontaneity of living things are occasionally conspicuous as well as inexplicable—is that they are keen to do their proper work; and their proper work is to pursue the laws of ordinary physical Energy into the intricacies of "colloidal electrolytic structures of great chemical complexity," and to study its behaviour there.

What we have clearly to grasp, on their testimony, is that for all the terrestrial manifestations of life the ordinary physical and chemical processes have to serve. There are not new laws for living matter, and old laws for non-living, the laws are the same; or if ever they differ, the burden of proof rests on him who sustains the difference. The conservation of energy, the laws of chemical combination, the laws of electric currents, of radiation, etc., etc.,—all the laws of Chemistry and Physics—may be applied without hesitation in the Organic domain. Whether they are sufficient is open to question, but as far as they go they are necessary; and it is the business of the physiologist to seek out and demonstrate the action of those laws in every vital action.

This is clearly recognised by the leaders, and in the definition of Physiology by Burdon Sanderson he definitely limited it to the study of "ascertainable characters of a chemical and physical type." In his Address to the Subsection of Anatomy and Physiology at York in 1881 he spoke as follows:—

> "It would give you a true idea of the nature of the great advance which took place about the middle of this century if I were to define it as the epoch of the death of 'vitalism.' Before that time, even the greatest biologists—*e.g.*, J. Müller—recognised that the knowledge biologists possessed both of vital and physical phenomena was insufficient to refer both to a common measure. The method therefore was to study the processes of life in relation to each other only. Since that time it has become fundamental in our science not to regard any vital process as understood at all unless it can be brought into relation with physical standards, and the methods of physiology have been based exclusively on this principle. The most efficient cause [conducing to the change] was the progress which had been made in physics and chemistry, and particularly those investigations which led to the establishment of the doctrine of the Conservation of Energy." . . . .
>
> "Investigators who are now working with such earnestness in all parts of the world for the advance of physiology, have before them a definite and well-understood purpose, that purpose being to acquire an exact knowledge of the chemical and physical processes of animal life and of the self-acting machinery by which they are regulated for the general good of the organism. The more singly and straightforwardly we direct our efforts to these ends, the sooner we shall attain to the still higher purpose—the effectual application of our knowledge for the increase of human happiness."

Professor Gotch, whose recent loss we have to deplore, puts it more strongly:—

> "It is essentially unscientific," he says, "to say that any physiological phenomenon is caused by vital force."

(To be continued)

A GENERAL METHOD FOR THE PREPARATION OF THE AMMONIUM SALTS OF ORGANIC ACIDS.

By EDWARD H. KEISER and L. McMASTER

THE usual method of preparing the ammonium salts of organic acids, namely, neutralising the aqueous solution of the acid with ammonia and evaporating to crystallisation, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts. A study of the literature of ammonium salts of organic acids shows that comparatively few of them have been made and analysed. In the case of dibasic acids usually only the acid ammonium salt has been prepared.

In attempting to prepare the amide of maleic acid we desired to start with the diammonium maleate, but found it impossible to make this salt by neutralising a solution of maleic acid with ammonia and evaporating to crystallisation. We therefore dissolved the acid in ether and conducted a stream of dry ammonia gas into the ethereal solution. A white flocculent rather gelatinous precipitate at first formed, this soon collected into lumps, and, on continuing to pass in ammonia, changed into a white crystalline powder. Analysis showed it to be diammonium maleate.

This method of preparing diammonium maleate was found to be applicable in a general way to the preparation of the ammonium salts of other organic acids. In those cases in which the acid was insoluble in ether some other solvent, such as absolute alcohol, or a mixture of ether and alcohol, was used. The method is dependent upon the fact that most organic acids are soluble in ether or alcohol or a mixture of the two, while the ammonium salts are insoluble and can be thrown down by means of a stream of dry ammonia gas. Very good yields are obtained by this method. The organic salts of other weak bases, such as the salts of aniline, the amines, and other organic bases can, no doubt, be made in the same general way by doing away with aqueous solutions and using only alcoholic or ethereal solutions of both acid and base.

We have made, in this way, the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic, and phthalic acids.

Ammonium Maleate.—This salt was precipitated from the ethereal solution of the acid by a stream of dry ammonia, as described above, washed on the filter with ether, and dried in the air. It is a white crystalline powder, not deliquescent in the air but readily soluble in water. Büchner (*Liebig's Ann. Chem.*, xlix., 67) describes this salt as being deliquescent, but his compound was prepared in the wet way. This salt has an odour similar to that of acetamide.

Analyses gave the following results:—

	C.	H.	N.
Calculated for $C_2H_2(CO_2NH_4)_2$	31·97	6·71	18·66
Found—I.	—	—	16·12
II.	31·20	7·09	16·13
III.	32·04	6·89	18·70
IV.	32·06	6·91	18·46

The first two nitrogen determinations were made by the Kjeldahl method and gave low results, the last two by the Dumas method. We also prepared this salt by precipitation with ammonia in a solution of the acid in absolute alcohol.

Ammonium Fumarate.—Fumaric acid was dissolved in absolute alcohol and dry ammonia conducted into the solution. A heavy white amorphous powder was at once formed. It was filtered, washed thoroughly with alcohol and ether, and dried in air on a porous plate. This salt has no odour, as in the case of the diammonium maleate. It is not deliquescent, but dissolves readily in water. It gave on analysis the following results :—

N calculated for $C_2H_2(CO_2NH_4)_2$.. ..	18·66
Found—I..	18·47
II..	18·50

Ammonium Mesaconate.—The mesaconic acid, obtained from Kahlbaum, was dissolved in ether and dry ammonia conducted into the solution. A gelatinous precipitate was at first formed, but this soon changed into a crystalline powder. The salt was filtered, washed on the filter with ether, and then dried in the air. Like the ammonium fumarate it had no odour. It was not deliquescent, but dissolved readily in water. Determinations of nitrogen gave the following results :—

N calculated for $CH_3C_2H(CO_2NH_4)_2$..	17·07
Found—I..	16·71
II..	16·84

Ammonium Citraconate.—Citraconic acid (Kahlbaum) was dissolved in ether and ammonia passed into the solution. A thick colloidal solution was at first formed, but as the ammonia continued to pass into the solution this changed into a crystalline precipitate. This was filtered, washed with ether, and dried in the air. Like the ammonium maleate it has an odour like that of acetamide. The salt is not deliquescent, but soluble in water.

N calculated for $CH_3C_2H(CO_2NH_4)_2$..	17·07
Found—I..	16·82
II..	16·87

The ammonium salts of malonic and phthalic acids were also made by the same general method. The ammonium malonate came down in ether solution as a fine white crystalline precipitate. It had no odour and was not deliquescent, although readily soluble in water. The ammonium phthalate was obtained as a white powder.—*American Chemical Journal*, xlix., No. 2.

NOTICES OF BOOKS.

Outline of Stationery Testing. By Henry Aldous Bromley. London: Charles Griffin and Co., Ltd. 1913.

This book gives a concise account of practical methods of testing stationery, and the author's experience as assistant examiner of paper to His Majesty's Stationery Office enables him to write authoritatively; and gives great weight to his hints and recommendations. No matter of purely theoretical interest is included in the book, which is intended specially for practical men, and only simple apparatus and methods are described, which, however, may be relied upon to give accurate results. The testing of paper by physical means is first discussed, and the Schopper and other machines which are used for determining the strength of paper are described and illustrated. In the chapter on microscopical methods plates showing the different fibres are given, with brief directions for the preparation and staining of specimens for examination. The chemical investigation of paper is treated in outline, and some notes are given on the characteristics and requirements of special papers. Other products, the testing of which is described, include inks, sealing-wax, string, and gums.

Report of the Woburn Experimental Station. I. *Field Experiments*, 1912. II. *Pot-culture Experiments*, 1910, 1911, 1912. By J. Augustus Voelcker, M.A., B.Sc., Ph.D. London: John Murray. 1913.

In this report the conclusions to be drawn from the field experiments conducted by the Woburn Experimental Station of the Royal Agricultural Society of England during 1912, the thirty-sixth consecutive season, are concisely stated. The experiments dealt with the continuous growing of wheat and barley, different varieties of cereals, the inoculation of leguminous crops, &c. The yield and quality of grain were in all cases below the average, although the root crops were unusually satisfactory. The more interesting part of the report is that which describes the Hills experiments upon the influence of the comparatively rare constituents of the soil upon wheat. As the result of several years' work it has been found that the salts of lithium exercise a stimulating effect, when the quantity present does not exceed 0·002 per cent. Above 0·003 per cent they are toxic in their action, the toxicity differing with different salts. Similar experiments with zinc salts give the same results, although their influence is very much less than that of lithium, and the general conclusion to be drawn from the whole series of experiments is that the influence of the rarer constituents of the soil upon vegetation is much greater than has hitherto been supposed.

The London Matriculation Directory, June, 1913. London: University Tutorial Press, Ltd.

This is the Sixty-fourth Number of the "London Matriculation Directory," and exhibits the same excellent features as those which have distinguished the earlier numbers. These include articles on the text-books in each subject, and hints to intending candidates as to the choice of subjects; the papers set in June, 1913, are reproduced in full, with solutions and criticisms of them, and in addition full information is given relating to the University Correspondence and Tutorial Colleges.

Science Conspectus. Vol. III., No. 3. Published by the Society of Arts of the Massachusetts Institute of Technology, Boston, Mass.

The aim of this periodical is to give a general survey of scientific work for educated readers who wish to keep abreast of recent advances in all branches. Most of the papers in this number are original, and are contributed by experts. They treat of such subjects as the importance of negative eugenics, the clam industry in Massachusetts, the Pyramids as an astronomical monument. Chemical science is represented by an interesting article on catalysis, in which the essential features of the phenomenon are described, and some possible explanations of its occurrence are put before the reader.

Notes on the Therapeutics of Radium in the Bath Waters. Compiled by John Hatton.

This handbook, published by the Corporation of Bath, has been compiled in order to place before the medical profession and the general public the results of recent investigations of the Hot Springs of Bath. It contains the report of Sir William Ramsay, in which the results of the analysis of the waters are stated, and suggestions are given of fresh methods of using the highly radio-active gas dissolved in the water. Other papers in the book are by Prof. Weiss on "The Balneological Aspect of Radium," and on "Radium Emanation and Physiological Processes," by Dr. S. Saubermann, and a brief list is given of the cases for which the waters of Bath are indicated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 25, June 23, 1913.

Phenomenon of Photocatalysis.—Max Landau.—Millinormal oxalic acid when exposed to the ultra-violet rays is decomposed 300 times more slowly than when exposed in presence of uranyl nitrate in equimolecular concentration. All compounds of uranium possess photocatalytic powers, and there is no parallelism between the photocatalytic power and the radio-active power of these compounds. Photocatalysis takes place even when the catalysts are insoluble, and the action is due exclusively to the cation. Some other metals were tested for the same power, but it was found that none of them was as strong as uranium.

Melting-points, Specific Heats, and Heats of Fusion of the Alkali Metals.—E. Rengade.—Very carefully performed determinations show that the atomic specific heats of the alkali metals increase slightly and regularly with the atomic weights, while the atomic heats of fusion decrease regularly. The ratio of the atomic heat of fusion to the absolute temperature of fusion is absolutely constant.

Oxidation of Alcohols under the Influence of Heat Alone.—J. B. Senderens.—When the temperature is raised the alcohols begin to undergo oxidation, the process beginning at 380° for amyl alcohol, 400° for isobutyl alcohol, and 405° for ethyl alcohol. All the oxygen of the air is absorbed by these alcohols at 410°, 435°, and 450° respectively. The chief product is CO, and a small amount of CO_2 is formed also. Certain substances such as magnesium, zinc, and aluminium, which have been supposed to be good catalysts, in reality act catalytically to only a very slight extent.

New Series of Isopyrazolones.—G. Favrel.—When dilute solutions of soda act on the hydrazones of the γ-chlorinated acetyl acetic ethers the latter are converted into isopyrazolones of a new type, which may be called 4-isopyrazolones. The γ-brominated acetyl acetic ethers give the same results, but with more difficulty.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 9, 1913.

New Hydrogen Boride, B_2H_6.—Alfred Stock and Kurt Friederici.—If gaseous hydrogen boride, B_4H_{10}, is kept for some time at room temperature over mercury the volume increases, and solid and gaseous products are obtained. The latter consist of hydrogen and a new boride, boiling at −87°, and having the formula B_2H_6. A convenient way to prepare the latter is to heat B_4H_{10} to 100° for some hours. It is a colourless gas of characteristic odour which recalls that of B_4H_{10}, and also of sulphuretted hydrogen. Its melting-point lies below −140°. It is much more stable than B_4H_{10}. When heated over an open flame it decomposes, giving colourless and yellow solid borides. It is decomposed by ultra-violet light and rapidly attacked by water, the following reaction occurring:—$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. It does not ignite in air unless other hydrogen borides are present.

Sensitiveness to Light of the Nitrides of Silver, Mercurous Oxide, Lead, Cuprous Oxide, and of Basic Lead and Cupric Nitrides.—Lothar Wöhler and W. Krupko.—Silver nitride is very sensitive to light, and nitrogen is evolved when coloured products are produced in sun or mercury light. The sensitiveness of the product to a blow or to rise of temperature shows that it is not a new subnitride, but a mixture of unchanged normal nitride with finely divided metal of a colloidal nature. The meta can be detected microphotographically, especially the mercury drops from mercurous nitride. Cuprous nitride, which the authors have prepared for the first time, shows the same sensitiveness to light. Considerable quantities of ammonia are formed when lead nitride is exposed to light under water, owing to hydrolysis and the reduction of the acid by metallic lead. By heating lead or copper nitride with the hydroxide under water, basic nitrides, $PbOPbN_6$ and $CuOCuN_6$ are formed.

MISCELLANEOUS.

Schools of Chemistry.—The following additional information has been received:—

MANCHESTER SCHOOL OF TECHNOLOGY.—The School is established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science (B.Sc. Tech. and M.Sc. Tech.). Special facilities are offered to graduate students desirous of pursuing advanced research in any department of Applied Chemistry and other branches of the Industrial Arts, and a Journal is published embodying the more important results of such researches. The possession of a University Degree is of increasing importance to young men who are seeking the more important positions connected with the Chemical Industries. The supply of students entering the Chemical Department, although it has been steadily increasing for some years, has not kept pace with the demand for those who have completed the degree course. Thus the number of applications for young men who have graduated in Chemistry from the School of Technology was last year much in excess of the number of students graduating in this department. A similar excess of the demand over the supply is now being experienced in the Electrical Engineering Department, while the demand on the part of Mechanical Engineering firms for graduates in Mechanical Engineering is also making itself felt.

LEEDS: CENTRAL TECHNICAL SCHOOL, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by W. W. Burrell, M.Sc., J. B. Murray, A. McFarlane, and G. H. Rydall, B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by B. A. Burrell, F.I.C., F.C.S., and T. O. Thornton; Gas Manufacture, by W. E. Petrigrew; Oils and Fats; Magnetism and Electricity, Practical Physics, &c., by J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by W. H. Quinn and J. C. Hesselgrave; Photography and Process Work, by S. E. Bottomley and others. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three-evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S; and N. Walker. Session commences Sept. 22nd. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to James Graham, Secretary for Education, Calverley Street, Leeds.

Hydrogenation of Santoninic Acid.—Guido Cusmano.—When sodium santoninate is hydrogenated in presence of platinum-black the product of the reaction is tetrahydrosantoninic acid, $C_{15}H_{24}O_4$. This dissolves in carbonates in the cold, gives no coloration with alcoholic potash, and has not the bitter taste of santonin. It dissolves easily in concentrated hydrochloric acid, giving a greenish brown solution, and when heated in alcoholic solution with hydroxylamine hydrochloride yields an oxime.—*Atti della Reale Accademia dei Lincei*, xxii., No. 8.

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Birmingham, 1913.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Oliver Lodge, D.Sc., LL.D., F.R.S., &c.

CONTINUITY.

Natura non vincitur nisi parendo.

(Concluded from p. 136).

I observe that by some critics I have been called a vitalist, and in a sense I am; but I am not a vitalist if vitalism means an appeal to an undefined "vital force" (an objectionable term I have never thought of using) as against the laws of Chemistry and Physics. Those laws must be supplemented, but need by no means be superseded. The business of science is to trace out their mode of action everywhere, as far and as fully as possible; and it is a true instinct which resents the mediæval practice of freely introducing spiritual and unknown causes into working science. In science an appeal to occult qualities must be illegitimate, and be a barrier to experiment and research generally; as, when anything is called an Act of God—and when no more is said. The occurrence is left unexplained. As an ultimate statement such a phrase may be not only true but universal in its application. But there are always proximate explanations which may be looked for and discovered with patience. So, lightning, earthquakes, and other portents are reduced to natural causes. No ultimate explanation is ever attained by science; proximate explanations only. They are what it exists for; and it is the business of scientific men to seek them.

To attribute the rise of sap to vital force would be absurd, it would be giving up the problem and stating nothing at all. The way in which osmosis acts to produce the remarkable and surprising effect is discoverable and has been discovered.

So it is always in science, and its progress began when unknown causes were eliminated and treated as non-existent. Those causes, so far as they exist, must establish their footing by direct investigation and research; carried on in the first instance apart from the long recognised branches of science, until the time when they too have become sufficiently definite to be entitled to be called scientific. Outlandish Territories may in time be incorporated as States, but they must make their claim good and become civilised first.

It is well for people to understand this definite limitation of scope quite clearly, else they wrest the splendid work of biologists to their own confusion,—helped it is true by a few of the more robust or less responsible theorisers, among those who should be better informed and more carefully critical in their philosophising utterances.

But, as is well known, there are more than a few biologists who, when taking a broad survey of their subject, clearly perceive and teach that before all the actions of live things are fully explained, some hitherto excluded causes must be postulated. Ever since the time of J. R. Mayer it has been becoming more and more certain that, as regards performance of work, a living thing obeys the laws of physics, like everything else; but undoubtedly it initiates processes and produces results that without it could not have occurred,—from a bird's nest to a honeycomb, from a deal box to a warship. The behaviour of a ship firing shot and shell is explicable in terms of energy, but the discrimination which it exercises between friend and foe is not so explicable. There is plenty of physics and chemistry and mechanics about every vital action, but for a complete understanding of it something beyond physics and chemistry is needed.

And life introduces an incalculable element. The vagaries of a fire or a cyclone could all be predicted by Laplace's Calculator, given the initial positions, velocities, and the law of acceleration of the molecules; but no mathematician could calculate the orbit of a common-house-fly. A physicist into whose galvanometer a spider had crept would be liable to get phenomena of a kind quite inexplicable, until he discovered the supernatural, *i.e.*, literally superphysical, cause. I will risk the assertion that Life introduces something incalculable and purposeful amid the laws of physics; it thus distinctly supplements those laws, though it leaves them otherwise precisely as they were and obeys them all.

We see only its effect, we do not see Life itself. Conversion of Inorganic into Organic is effected always by living organisms. The conversion under those conditions certainly occurs, and the process may be studied. Life appears necessary to the conversion; which clearly takes place under the guidance of life, though in itself it is a physical and chemical process. Many laboratory conversions take place under the guidance of life, and, but for the experimenter, would not have occurred.

Again, putrefaction, and fermentation, and purification of rivers, and disease, are not purely and solely chemical processes. Chemical processes they are, but they are initiated and conducted by living organisms. Just when medicine is becoming biological, and when the hope of making the tropical belt of the earth healthily habitable by energetic races is attracting the attention of people of power, philosophising biologists should not attempt to give their science away to Chemistry and Physics. Sections D and H and I and K are not really subservient to A and B. Biology is an independent science, and it is served, not dominated, by Chemistry and Physics.

Scientific men are hostile to superstition, and rightly so, for a great many popular superstitions are both annoying and contemptible; yet occasionally the term may be wrongly applied to practices of which the theory is unknown. To a superficial observer some of the practices of biologists themselves must appear grossly superstitious. To combat malaria Sir Ronald Ross does not indeed erect an altar; no, he oils a pond,—making libation to its presiding genii. What can be more ludicrous than the curious and evidently savage ritual, insisted on by United States Officers, at that hygienically splendid achievement the Panama Canal,—the ritual of punching a hole in every discarded tin, with the object of keeping off disease! What more absurd, again,—in superficial appearance—than the practice of burning or poisoning a soil to make it extra fertile!

Biologists in their proper field are splendid, and their work arouses keen interest and enthusiasm in all whom they guide into their domain. Most of them do their work by intense concentration, by narrowing down their scope, not by taking a wide survey or a comprehensive grasp. Suggestions of broader views and outlying fields of knowledge seem foreign to the intense worker, and he resents them. For his own purpose he wishes to ignore them, and practically he may be quite right. The folly of negation is not his, but belongs to those who misinterpret or misapply his utterances, and take him as a guide in a region where, for the time at least, he is a stranger. Not by such aid is the universe in its broader aspects to be apprehended. If people in general were better acquainted with science they would not make these mistakes. They would realise both the learning and the limitations, make use of the one and allow for the other, and not take the recipe of a practical worker for a formula wherewith to interpret the Universe.

What appears to be quite certain is that there can be no

terrestrial manifestation of life without matter. Hence naturally they say, or they approve such sayings as, "I discern in matter the promise and potency of all forms of life." Of all terrestrial manifestations of life, certainly. How else could it manifest itself save through matter? "I detect nothing in the organism but the laws of Chemistry and Physics," it is said. Very well: naturally enough. That is what they are after; they are studying the physical and chemical aspects or manifestations of life. But life itself—life and mind and consciousness—they are not studying, and they exclude them from their purview. Matter is what appeals to our senses here and now; Materialism is appropriate to the material world; not as a philosophy but as a working creed, as a proximate and immediate formula for guiding research. Everything beyond that belongs to another region, and must be reached by other methods. To explain the Psychical in terms of Physics and Chemistry is simply impossible; hence there is a tendency to deny its existence, save as an epiphenomenon. But all such philosophising is unjustified, and is really bad Metaphysics.

So if ever in their enthusiasm scientific workers go too far and say that the things they exclude from study have no existence in the universe, we must appeal against them to direct experience. We ourselves are alive, we possess life and mind and consciousness, we have first hand experience of these things quite apart from laboratory experiments. They belong to the common knowledge of the race. Births, deaths, and marriages are not affairs of the biologist, but of humanity; they went on before a single one of them was understood, before a vestige of science existed. We ourselves are the laboratory in which men of science, psychologists, and others, make experiments. They can formulate our processes of digestion, and the material concomitants of willing, of sensation, of thinking; but the hidden guiding entities they do not touch.

So also if any philosopher tells you that you do not exist, or that the external world does not exist, or that you are an automaton without free will, that all your actions are determined by outside causes, and that you are not responsible,—or that a body cannot move out of its place, or that Achilles cannot catch a tortoise—then in all those cases appeal must be made to twelve average men, unsophisticated by special studies. There is always a danger of error in interpreting experience, or in drawing inferences from it; but in a matter of bare fact, based on our own first-hand experience, we are able to give a verdict. We may be mistaken as to the nature of what we see. Stars may look to us like bright specks in a dome, but the fact that we see them admits of no doubt. So also Consciousness and Will are realities of which we are directly aware, just as directly as we are of motion and force, just as clearly as we apprehend the philosophising utterances of an Agnostic. The process of seeing, the plain man does not understand; he does not recognise that it is a method of etherial telegraphy; he knows nothing of the ether and its ripples, nor of the retina and its rods and cones, nor of nerve and brain processes; but he sees and he hears and he touches, and he wills and he thinks and is conscious. This is not an appeal to the mob as against the philosopher, it is appeal to the experience of untold ages as against the studies of a generation.

How consciousness became associated with matter, how life exerts guidance over chemical and physical forces, how mechanical motions are translated into sensations—all these things are puzzling and demand long study. But the fact that these things are so admits of no doubt; and difficulty of explanation is no argument against them. The blind man restored to sight had no opinion as to how he was healed, nor could he vouch for the moral character of the Healer, but he plainly knew that whereas he was blind now he saw. About that fact he was the best possible judge. So it is also with "this main miracle that thou art thou, With power on thine own act and on the world."

But although Life and Mind may be excluded from Physiology, they are not excluded from Science. Of course not. It is not reasonable to say that things necessarily elude investigation merely because we do not knock against them. Yet the mistake is sometimes made. The ether makes no appeal to sense, therefore some are beginning to say that it does not exist. Mind is occasionally put into the same predicament. Life is not detected in the laboratory, save in its physical and chemical manifestations; but we may have to admit that it guides processes nevertheless. It may be called a catalytic agent.

To understand the action of life itself, the simplest plan is not to think of a microscopic organism, or any unfamiliar animal, but to make use of our own experience as living beings. Any positive instance serves to stem a comprehensive denial, and if the reality of mind and guidance and plan is denied because they make no appeal to sense, then think how the world would appear to an observer to whom the existence of men was unknown and undiscoverable, while yet all the laws and activities of nature went on as they do now.

Suppose, then, that *man* made no appeal to the senses of an observer of this planet. Suppose an outside observer could see all the events occurring in the world, save only that he could not see animals or men. He would describe what he saw much as we have to describe the activities initiated by life.

If he looked at the Firth of Forth, for instance, he would see piers arising in the water, beginning to sprout, reaching across in strange manner till they actually join or are joined by pieces attracted up from below to complete the circuit (a solid circuit round the current). He would see a sort of bridge or filament thus constructed, from one shore to the other, and across this bridge insect-like things crawling and returning for no very obvious reason.

Or let him look at the Nile, and recognise the meritorious character of that river in promoting the growth of vegetation in the desert. Then let him see a kind of untoward crystallisation growing across and beginning to dam the beneficent stream. Blocks fly to their places by some kind of polar forces; "we cannot doubt" that it is by helio- or other tropism. There is no need to go outside the laws of mechanics and physics, there is no difficulty about supply of energy—none whatever—materials in tin cans are consumed which amply account for all the energy; and all the laws of physics are obeyed. The absence of any design, too, is manifest; for the effect of the structure is to flood an area up-stream which might have been useful, and to submerge a structure of some beauty; while down stream its effect is likely to be worse, for it would block the course of the river and waste it on the desert, were it not that fortunately some leaks develop and a sufficient supply still goes down—goes down in fact more equably than before; so that the ultimate result is beneficial to vegetation, and simulates intention.

If told concerning either of these structures that an engineer, a designer in London, called Benjamin Baker, had anything to do with it, the idea would be preposterous. One conclusive argument is final against such a superstitious hypothesis—he is not there, and a thing plainly cannot act where it is not. But although we, with our greater advantages, perceive that the right solution for such an observer would be the recognition of some unknown agency or agent, it must be admitted that an explanation in terms of a vague entity called vital force would be useless, and might be so worded as to be misleading; whereas a statement in terms of mechanics and physics could be clear and definite and true as far as it went, though it must necessarily be incomplete.

And note that what we observe, in such understood cases, is an *Interaction* of Mind and Matter; not Parallelism nor Epiphenomenalism nor anything strained or difficult, but a straightforward utilisation of the properties of matter and energy for purposes conceived in the mind, and executed by muscles guided by acts of will.

But, it will be said, this is unfair, for we *know* that

there is design in the Forth Bridge or the Nile Dam, we have seen the plans and understand the agencies at work; we know that it was conceived and guided by life and mind, it is unfair to quote this as though it could simulate an automatic process.

Not at all, say the extreme school of biologists whom I am criticising, or ought to say if they were consistent, there is nothing but Chemistry and Physics at work anywhere; and the mental activity apparently demonstrated by those structures is only an illusion, an epiphenomenon; the laws of chemistry and physics are supreme, and they are sufficient to account for everything!

Well, they account for things up to a point; they account in part for the colour of a sunset, for the majesty of a mountain peak, for the glory of animate existence. But do they account for everything completely? Do they account for our own feeling of joy and exultation, for our sense of beauty, for the manifest beauty existing throughout nature? Do not these things suggest something higher and nobler and more joyous, something for the sake of which all the struggle for existence goes on?

Surely there must be a deeper meaning involved in natural objects. Orthodox explanations are only partial, though true as far as they go. When we examine each particoloured pinnule in a peacock's tail, or hair in a zebra's hide, and realise that the varying shades on each are so placed as to contribute to the general design and pattern, it becomes exceedingly difficult to explain how this organised co-operation of parts, this harmonious distribution of pigment cells, has come about on merely mechanical principles. It would be as easy to explain the sprouting of the cantilevers of the Forth Bridge from its piers, or the flocking of the stones of the Nile Dam by chemiotaxis. Flowers attract insects for fertilisation; and fruit tempts animals to eat it in order to carry seeds. But these explanations cannot be final. We have still to explain the insects. So much beauty cannot be necessary merely to attract their attention. We have further to explain this competitive striving towards life. Why do things struggle to exist? Surely the effort must have some significance, the development some aim. We thus reach the problem of Existence itself, and the meaning of Evolution.

The mechanism whereby existence entrenches itself is manifest, or at least has been to a large extent discovered. Natural Selection is a vera causa, so far as it goes; but if so much beauty is necessary for insects, what about the beauty of a landscape or of clouds? What utilitarian object do those subserve? Beauty in general is not taken into account by science. Very well, that may be all right, but it exists nevertheless. It is not my function to discuss it. No; but it is my function to remind you and myself that our studies do not exhaust the universe, and that if we dogmatise in a negative direction, and say that we can reduce everything to physics and chemistry, we gibbet ourselves as ludicrously narrow pedants, and are falling far short of the richness and fullness of our human birthright. How far preferable is the reverent attitude of the Eastern Poet:—

> "The world with eyes bent upon thy feet stands in awe with all its silent stars."

Superficially and physically we are very limited. Our sense organs are adapted to the observation of matter; and nothing else directly appeals to us. Our nerve-muscle system is adapted to the production of motion in matter, in desired ways; and nothing else in the material world can we accomplish. Our brain and nerve systems connect us with the rest of the physical world. Our senses give us information about the movements and arrangements of matter. Our muscles enable us to produce changes in those distributions. That is our equipment for human life; and human history is a record of what we have done with these parsimonious privileges.

Our brain, which by some means yet to be discovered connects us with the rest of the material world, has been thought partially to disconnect us from the mental and spiritual realm, to which we really belong but from which for a time and for practical purposes we are isolated. Our common or social association with matter gives us certain opportunities and facilities, combined with obstacles and difficulties which are themselves opportunities for struggle and effort.

Through matter we become aware of each other, and can communicate with those of our fellows who have ideas sufficiently like our own for them to be stimulated into activity by a merely physical process set in action by ourselves. By a timed succession of vibratory movements (as in speech and music), or by a static distribution of materials (as in writing, painting, and sculpture), we can carry on intelligent intercourse with our fellows; and we get so used to these ingenious and roundabout methods, that we are apt to think of them and their like as not only the natural but as the only possible modes of communication, and that everything more direct would disarrange the whole fabric of science.

It is clearly true that our bodies constitute the normal means of manifesting ourselves to each other while on the planet; and that if the physiological mechanism whereby we accomplish material acts is injured, the conveyance of our meaning and the display of our personality inevitably and correspondingly suffer.

So conspicuously is this the case that it has been possible to suppose that the communicating mechanism, formed and worked by us, is the whole of our existence; and that we are essentially nothing but the machinery by which we are known. We find the machinery utilising nothing but well-known forms of energy, and subject to all the laws of chemistry and physics—it would be strange if it were not so—and from that fact we try to draw valid deductions as to our nature, and as to the impossibility of our existing apart from and independent of these temporary modes of material activity and manifestation. We so uniformly employ them, in our present circumstances, that we should be on our guard against deception due to this very uniformity. Material bodies are all that we have any control over, are all that we are experimentally aware of; anything that we can do with these is open to us; any conclusions we can draw about them may be legitimate and true. But to step outside their province and to deny the existence of any other region because we have no sense organ for its appreciation, or because (like the Ether) it is too uniformly omnipresent for our ken, is to wrest our advantages and privileges from their proper use and apply them to our own misdirection.

But if we have learnt from science that Evolution is real, we have learnt a great deal. I must not venture to philosophise, but certainly from the point of view of science Evolution is a great reality. Surely evolution is not an illusion; surely the universe progresses in time. Time and Space and Matter are abstractions, but are none the less real: they are data given by experience; and Time is the keystone of evolution. "Thy centuries follow each other, perfecting a small wild flower."

We abstract from living moving Reality a certain static aspect, and we call it Matter; we abstract the element of progressiveness, and we call it Time. When these two abstractions combine, co-operate, interact, we get reality again. It is like Poynting's theorem.

The only way to refute or confuse the theory of Evolution is to introduce the subjectivity of time. That theory involves the reality of time, and it is in this sense that Prof. Bergson uses the great phrase "Creative Evolution."

I see the whole of material existence as a steady passage from past to future, only the single instant which we call the present being actual. The past is not non-existent, however, it is stored in our memories, there is a record of it in matter, and the present is based upon it; the future is the outcome of the present, and is the product of evolution.

Existence is like the output from a loom. The pattern, the design for the weaving, is in some sort "there" already;

but whereas our looms are mere machines, once the guiding cards have been fed into them, the Loom of Time is complicated by a multitude of free agents who can modify the web, making the product more beautiful or more ugly according as they are in harmony or disharmony with the general scheme. I venture to maintain that manifest imperfections are thus accounted for, and that *freedom* could be given on no other terms, nor at any less cost.

The ability thus to work for weal or woe is no illusion, it is a reality, a responsible power which conscious agents possess; wherefore the resulting fabric is not something preordained and inexorable, though by wide knowledge of character it may be inferred. Nothing is inexorable except the uniform progress of time; the cloth must be woven, but the pattern is not wholly fixed and mechanically calculable.

Where inorganic matter alone is concerned, there everything is determined. Wherever full consciousness has entered, new powers arise, and the faculties and desires of the conscious parts of the scheme have an effect upon the whole. It is not guided from outside but from within; and the guiding power is immanent at every instant. Of this guiding power we are a small but not wholly insignificant portion.

That evolutionary progress is real is a doctrine of profound significance, and our efforts at social betterment are justified because we are a part of the scheme, a part that has become conscious, a part that realises, dimly at any rate, what it is doing and what it is aiming at. Planning and aiming are therefore not absent from the whole, for we are a part of the whole, and are conscious of them in ourselves.

Either we are immortal beings or we are not. We may not know our destiny, but we must have a destiny of some sort. Those who make denials are just as likely to be wrong as those who make assertions; in fact, denials are assertions thrown into negative form. Scientific men are looked up to as authorities, and should be careful not to mislead. Science may not be able to reveal human destiny, but it certainly should not obscure it. Things are as they are, whether we find them out or not; and if we make rash and false statements, posterity will detect us—if posterity ever troubles its head about us. I am one of those who think that the methods of Science are not so limited in their scope as has been thought; that they can be applied much more widely, and that the Psychic region can be studied and brought under law too. Allow us anyhow to make the attempt. Give us a fair field. Let those who prefer the materialistic hypothesis by all means develop their thesis as far as they can; but let us try what we can do in the Psychical region, and see which wins. Our methods are really the same as theirs—the subject-matter differs. Neither should abuse the other for making the attempt.

Whether such things as intuition and revelation ever occur is an open question. There are some who have reason to say that they do. They are at any rate not to be denied off-hand. In fact, it is always extremely difficult to deny *anything* of a general character, since evidence in its favour may be only hidden and not forthcoming, especially not forthcoming at any particular age of the world's history, or at any particular stage of individual mental development. Mysticism must have its place, though its relation to Science has so far not been found. They have appeared disparate and disconnected, but there need be no hostility between them. Every kind of reality must be ascertained and dealt with by proper methods. If the voices of Socrates and of Joan of Arc represent real psychical experiences, they must belong to the intelligible universe.

Although I am speaking ex cathedra, as one of the representatives of orthodox science, I will not shrink from a personal note summarising the result on my own mind of thirty years' experience of psychical research, begun without predilection—indeed with the usual hostile preudice. This is not the place to enter into details or to discuss facts scorned by orthodox science, but I cannot help remembering that an utterance from this Chair is no ephemeral production, for it remains to be criticised by generations yet unborn, whose knowledge must inevitably be fuller and wider than our own. Your President therefore should not be completely bound by the shackles of present-day orthodoxy, nor limited to beliefs fashionable at the time. In justice to myself and my co-workers I must risk annoying my present hearers, not only by leaving on record our conviction that occurrences now regarded as occult can be examined and reduced to order by the methods of science carefully and persistently applied, but by going further and saying, with the utmost brevity, that already the facts so examined have convinced me that memory and affection are not limited to that association with matter by which alone they can manifest themselves here and now, and that personality persists beyond bodily death. The evidence to my mind goes to prove that discarnate intelligence, under certain conditions, may interact with us on the material side, thus indirectly coming within our scientific ken; and that gradually we may hope to attain some understanding of the nature of a larger, perhaps etherial, existence, and of the conditions regulating intercourse across the chasm. A body of responsible investigators have even now landed on the treacherous but promising shores of a new continent.

Yes, and there is more to say than that. The methods of science are not the only way, though they are our way, of arriving at truth. "*Uno itinere non potest perveniri ad tam grande secretum.*"

Many scientific men still feel in pugnacious mood towards Theology, because of the exaggerated dogmatism which our predecessors encountered and overcame in the past. They had to struggle for freedom to find truth in their own way; but the struggle was a miserable necessity, and has left some evil effects. And one of them is this lack of sympathy, this occasional hostility, to other more spiritual forms of truth. We cannot really and seriously suppose that truth began to arrive on this planet a few centuries ago. The pre-scientific insight of genius—of Poets and Prophets and Saints—was of supreme value, and the access of those inspired seers to the heart of the universe was profound. But the camp followers, the scribes and pharisees, by whatever name they may be called, had no such insight, only a vicious or a foolish obstinacy; and the prophets of a new era were stoned.

Now at last we of the new era have been victorious; we inherit the fruits of the age-long conflict, and the stones are in our hands. Let us not fall into the old mistake of thinking that ours is the only way of exploring the multifarious depths of the universe, and that all others are worthless and mistaken. The universe is a larger thing than we have any conception of, and no one method of search will exhaust its treasures.

Men and brethren, we are trustees of the truth of the physical universe as scientifically explored; let us be faithful to our trust.

Genuine religion has its roots deep down in the heart of humanity and in the reality of things. It is not surprising that by our methods we fail to grasp it; the actions of the Deity make no appeal to any special sense, only a universal appeal; and our methods are, as we know, incompetent to detect complete uniformity. There is a Principle of Relativity here, and unless we encounter flaw or jar or change, nothing in us responds; we are deaf and blind therefore to the immanent Grandeur around us, unless we have insight enough to appreciate the Whole, and to recognise in the woven fabric of existence, flowing steadily from the loom in an infinite progress towards perfection, the ever-growing garment of a transcendent God.

Summary of the Argument.

A marked feature of the present scientific era is the discovery of, and interest in, various kinds of Atomism; so that Continuity seems in danger of being lost sight of.

Another tendency is toward comprehensive negative generalisations from a limited point of view.

Another is to take refuge in rather vague forms of statement, and to shrink from closer examination of the puzzling and the obscure.

Another is to deny the existence of anything which makes no appeal to organs of sense, and no ready response to laboratory experiment.

Against these tendencies the author contends. He urges a belief in ultimate continuity as essential to science; he regards scientific concentration as an inadequate basis for philosophic generalisation; he believes that obscure phenomena may be expressed simply if properly faced; and he points out that the non-appearance of anything perfectly uniform and omnipresent is only what should be expected, and is no argument against its real substantial existence.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

BIRMINGHAM, 1913.

By Prof. W. P. WYNNE, D.Sc., F.R.S., President of the Section.

When the present position of education in Birmingham is considered, the transformation effected since the 'seventies is little short of marvellous. Five-and-thirty years ago, when I became an evening student, classes conducted by the Midland Institute met the demand for Arts and Science subjects; now a University—venerable in comparison with all Civic Universities save the Victoria University of Manchester—exists to provide instruction in every branch of learning. The spacious building in which we meet—already too small for the demands made on it—is the lineal descendant of that part of the Midland Institute which formerly was used for evening class instruction in science, organised in connection with the Science and Art Department, and financed largely by the system of payment on results; this large lecture theatre replaces the small and inconvenient classroom in which the teaching of Chemistry and Physics under Mr. Woodward was carried on. Payment on results is obsolete, and the "May" examinations on which it was based have almost disappeared, assessment by inspection now replacing both; nevertheless, it is more than doubtful whether any other system—in the circumstances of the time—could have spread so widely a knowledge of science among the people, or prepared the way for the Technical Instruction Act, and that appreciation of the value of scientific training for industrial pursuits, which is exemplified by the provision through municipal agencies of Technical Schools in the industrial centres of this country. I sometimes think the Science and Art Department, and those great men, Sir John Donnelly and Professor Huxley, who did much to shape its attitude towards science instruction in evening classes and in the Science Schools at South Kensington (Note 1), have received something less than their share of credit for pioneering work which finds its fruition in well-equipped Institutions like this, and in the enhanced position which science holds to-day in the estimation of our countrymen. In those far-off times, before the foundation stone of Mason College was laid, such evening classes in Birmingham provided the only means by which instruction in science, or scholarships to South Kensington, could be obtained. It is not unfitting, therefore, that I—a product of the system—should acknowledge here the obligation under which I stand both to the Midland Institute and to the Science and Art Department for providing the ladder by which I have risen, however undeservedly, to the honourable position of President of this Section.

The historian of our times will not fail to note some of the consequences which have followed the application of science to industry, possibly also some of the educational results which have followed the development of science teaching in schools of all grades. Except from one point of view these need not concern us now as they fall, the one in so far as Chemistry is concerned, into the province of the Society of Chemical Industry, the other mainly within the purview of Section L. This bringing of Chemistry to the people has aroused a widespread interest in some aspects of the subject, of which the Press has not been slow to take note. Not even the heuristic method can hide from the schoolboy the fact that certain fundamental conceptions are accepted which do not admit of proof, such as the indivisible atom, the non-decomposable element, the indestructibility of matter. When therefore, as one of the first-fruits of his discovery that positive rays furnish the most delicate method of chemical analysis, Sir J. J. Thomson has obtained from the most diverse solids a new gas, X_3; and by a different procedure, Professor Collie with Mr. Patterson have discovered that hydrogen, under the influence of electric discharges at low pressure, becomes replaced by neon, helium, and a third gas which is possibly identical with X_3 (Note 2), it is not surprising that we should hear much about it in the newspapers, just as was the case when the disintegration of radium was in process of being established. Further investigation may fail to substantiate some of the views which have been expressed about this unexplained disappearance of hydrogen; the origin of the neon and helium which make their appearance in the tube as the experiments proceed; the source of the gas X_3. Fortunately X_3, unlike neon and helium, has some chemical properties—it disappears, for example, when violently exploded with a mixture of oxygen and hydrogen (Note 3)—but we do not yet know whether it is a new element with an atomic weight of about 3, or a compound of hydrogen with an element yet to be discovered. This much at least seems certain: it is not the gas which, according to Mendeleeff, should precede fluorine in the halogen series, but whether its discovery, like that of argon, will necessitate a revision of the Periodic Table of the elements we cannot know until the mystery which at present surrounds it has been dispelled.

It was in 1886, at the last meeting of this Association in Birmingham, that Sir William Crookes whose continued activities are a source of pride and gratification to his brother chemists—gave that famous Address in which, clothing his ideas in language which has something of the magic of word-painting, he traced the evolution of the elements, as we know them, from the hypothetical protyle or Urstoff. The common origin of all elementary substances is now an accepted theory, although the question whether the idea underlying the term "transmutation" is verifiable under available conditions is answered differently according to the view we take of the disintegration of radium and kindred phenomena. But no one could have imagined that before another Birmingham meeting, the Periodic Table to which Sir William Crookes devoted much attention would have been enriched not only by a series or elements devoid of chemical properties, but by a second series, known only in minute quantities, and displaying those extraordinary properties of radio-activity which have revolutionised our ideas in more than one direction.

It is not necessary for me to chronicle even the more striking achievements in chemistry since 1886; a few examples will show how great the progress has been. It is on record that Arrhenius was present at that meeting, but his advocacy of that theory of solutions with which his name will always be associated came a little later; phenylhydrazine, which was to play so important a part in Emil Fischer's investigation of the sugars, had been discovered by him only two years previously; the Grignard reagent, which in other directions has played a no less important part in synthetical organic chemistry, did not become available until some fourteen years later. Theories then emerging, such as that of geometrical isomerism, have

either been discarded or modified by the discovery of new facts, and who shall say that the ionic theory of dissociation stands where it did, now that ions in solution have incurred the suspicion of associating with the solvent, and to that extent have come into line with molecules, for the orthodox behaviour of which Professor Armstrong himself would no doubt be prepared to vouch.

Residual Valency.

Among the many doctrines which have suffered under the stress of long sustained investigation, that of valency is a prominent example. Valency is that property by which an atom attracts to itself other atoms or radicals, and its numerical value is deduced from the structural formulæ of compounds in which that atom occurs. Claus seems to have been the first to recognise that this attraction between two atoms is not a constant, but depends on the nature of the other atoms or radicals in the molecule (Note 4), and it is of interest to note in connection with what follows that he used methane and its chloro-derivatives to illustrate his point of view. Valency may vary, therefore, from compound to compound; it is known to alter under the influence of change in temperature, as, for example, when carbon dioxide or phosphorus pentachloride undergoes thermal dissociation. But Claus's view did not meet with ready acceptance; hence at the Birmingham Meeting few chemists, if any, would have questioned the quadrivalency of carbon, despite the difficulty caused by the existence of carbon monoxide. Now, carbon is believed to be bivalent in the carbamines, fulminic acid and other compounds as well as in carbon monoxide, and its tervalency is coming to be accepted in the light of the latest investigations on triphenylmethyl and its congeners. What is true of carbon is equally true of all other elements, except argon and its companions. Hence the doctrine of constant valency for which Kekulé contended, or that of variable valency in which the uncombined units varied by even numbers has necessarily given place to one of less rigid type, although the final form has yet to be determined.

For the purpose of this Address it will be sufficient to refer only to one of these later theories: that in which Werner, as the outcome of his exhaustive study of inorganic molecular compounds, and especially of the ammines, supposes that an atom may have both principal and auxiliary or residual valency (Note 5). There are difficulties in its application to certain problems of organic chemistry—for example, the structure of the benzene molecule—but the conspicuous success which has attended Werner's investigation of the complicated isomerism of the cobalt and chromium ammines is evidence of its value as a guide in stimulating research in the most unpromising directions (Note 6). Werner's view that valency is an attractive force acting from the centre of the atom, being of equal value at all points on the surface and independent of units of affinity, has the merit of meeting the objection long urged to the idea that affinity has fixed direction in space, but otherwise leaves untouched van't Hoff's brilliant conception of asymmetry which plays so great a part in the chemistry of to-day.

What light does this conception of residual valency, dating back to 1885, if not earlier (Note 7), and now embodied in many theories besides Werner's, throw on some of the problems with which the organic chemist is faced? Much every way. The question of the distribution of valency in the molecules of carbon compounds is discussed probably more than any other; it arises in connection with the structure of unsaturated compounds, the properties of fluorescence or colour which many of them exhibit, and the relation between chemical constitution and physical properties, to the elucidation of which an increasing amount of research is being directed. The double linkings in our formulæ no longer represent two units of valency in terms of hydrogen, nor are they now used to indicate polarity of the central atom or distribution of the valency in space; Werner's conception of valency accounts, as the phase goes, for the concentration of reactivity at that part of the molecule where unsaturation exists, and it is of service when different degrees of unsaturatedness are displayed by compounds which, on the older view, would be expected to show similarity in chemical behaviour (Note 8). With your permission I propose briefly to review our knowledge of that type of chemical change known as substitution from the standpoint of residual valency.

Substitution in the Paraffin Series.

So far back as 1839 the fact was discovered that replacement of hydrogen by chlorine in the acetic acid molecule does not lead to any essential modification in the properties of the acid. It is not a little remarkable therefore that although much of the progress in organic chemistry has been achieved by substitutions of the most diverse types, we are still unable to say that agreement has been reached with regard to the nature of the processes by which this replacement of one radical by another in a molecule is brought about. Never has attention been concentrated more closely than now on the study of what, for want of a better phrase, is termed the "mechanism of chemical reactions"—the processes which are covered and hidden by the sign of equality used, inaptly, in chemical equations—but the integrating mind, to the need for which Professor Frankland alluded on a recent occasion (Note 9), has not yet been evolved to reconcile the uncertain or contradictory answers vouchsafed to much patient experimenting. Organic chemistry is not singular in this respect; as much might be said about controversies not yet settled which concern themselves with such every-day phenomena as the chemistry of the candle-flame or of the rusting of iron.

It is a commonplace that Kekulé, to whom theoretical chemistry owes so many fruitful suggestions, was of the opinion that substitution is not a process in which what may be called a direct exchange of radicals occurs, but is preceded by the temporary union of the molecules of carbon compound and addendum, followed by disruption into two new molecules, the substituted carbon compound being one of them. It is clear, then, from the standpoint of Kekulé's hypothesis, that some degree of unsaturation is to be looked for in all carbon compounds and in all addenda. Hence, the paraffin hydrocarbons which furnish derivatives only by substitution, and under the older, more rigid view of valency propounded by Kekulé himself, are typically saturated compounds, supply the exceptions to prove the general validity of the hypothesis that addition precedes substitution.

Before examining the case of these hydrocarbons, however, some advantage may be gained if the behaviour of other groups of compounds be examined in the light of the idea underlying Kekulé's view. By reference to the literature, it is evident that since the beginning of this century attention has been concentrated on the phenomena of substitution in the important group of carbonyl compounds, particularly the ketones and acids, which in many cases yield halogen substitution derivatives of one type. Thus methyl ethyl ketone when brominated in sunlight yields two bromoketobutanes of the constitution shown in the following formulæ, and propionic acid with bromine and red phosphorus under Volhard's conditions (Note 10) gives α-bromopropionic acid,—

$CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ and $CH_3{\cdot}CO{\cdot}CHBr{\cdot}CH_3$ (Note 11)

$CH_3{\cdot}CHBr{\cdot}CO{\cdot}OH$,

the halogen occupying what is termed the α-position with reference to the carbonyl radical. Why is substitution easier in the methyl group when it is present in the ketone or acid than when it occurs in methane, is one question that may be asked. A second will inquire whether the carbonyl group has a directing influence, and, if so, by what means is it exercised.

It has been supposed by Werner that the distribution of valency is disturbed by the introduction of the oxygen atom of the carbonyl group into the molecule of the hydro-

carbon ; that this oxygen atom absorbs much of the valency of the carbon atom of the carbonyl group, leaving less to bind its neighbour or neighbours, which results in their having free valency, and thereby attaching substituents to themselves. This explanation, if accepted for the bromination of ketones and acids, also for the chlorination of ketones, does not account for the results recorded by Michael and by Montemartini in the case of carboxylic acids. Michael has found that the β-chloro, not the α-chloro, acid is the chief product (60—65 per cent) when homologues of acetic acid are chlorinated (Note 12) ; and Montemartini states that if the radical CH occur in any part of the carbon chain the exchange of hydrogen for chlorine takes place in that position, however distant it may be from the carbonyl group of the acid (Note 13).

$CH_3 \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot CO \cdot OH$
(Michael)

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CCl \cdot CH_2 \cdot CH_2 \cdot CO \cdot OH.$$
(Montemartini)

At present there seems to be no clue to the reason why chlorine and bromine in these reactions behave alike towards ketones and not towards acids.

An alternative explanation of this reaction, which has come to be widely accepted, is based on the remarkable property called desmotropy or dynamic isomerism, which certain of these carbonyl compounds exhibit. A desmotropic compound may exist in two or more forms, and its peculiar isomerism is known to depend on the mobility of a hydrogen atom in the complex $\cdot CH_2 \cdot CO \cdot$ whereby an equilibrium is set up of the type :—

$$\underset{\text{Ketonic form}}{\cdot CH_2 \cdot CO \cdot} \rightleftharpoons \underset{\text{Enolic form}}{\cdot CH{:}C(OH) \cdot}$$

Of these two forms, the enolic is the more unsaturated, and presumably the more reactive (Note 14). Lapworth, making use of this desmotropic relationship, supposes that when the ketone reacts with halogen in dilute aqueous solution three changes occur which, for the case of acetone, may be represented by the following expressions :—

$$CH_3 \cdot CO \cdot CH_3 \rightarrow CH_3 \cdot C(OH){:}CH_2$$
$$CH_3 \cdot C(OH){:}CH_2 + Br_2 \rightarrow CH_3 \cdot C(OH)Br \cdot CH_2Br.$$
$$CH_3 \cdot C(OH)Br \cdot CH_2Br \rightarrow CH_3 \cdot CO \cdot CH_2Br + HBr$$

the first being one of slow enolisation, accelerated catalytically by halogen acid, leading to the production of an unsaturated compound, which then by rapid addition of bromine and subsequent elimination of hydrogen bromide conforms with Kekulé's hypothesis. The intermediate compounds, it is true, have not been isolated, but a study of the dynamics of the reaction by Lapworth, and later by Dawson with his collaborators (using iodine instead of bromine), shows that this explanation is in harmony with the data obtained (Note 15). When the reaction is applied to carboxylic acids under similar conditions, the view that it takes a similar course finds support from an investigation of the dynamics of the bromination of malonic acid in aqueous solution (Note 16).

Whether evidence drawn from reactions found to take place in aqueous solution is relevant when bromination is effected by heating a carboxylic acid with bromine and red phosphorus may be doubted. Certainly it seems to afford no assistance in accounting for the course of chlorination in the acids examined by Michael and by Montemartini. Nevertheless, Aschan employs the keto-enolic hypothesis (Note 17) to elucidate the results of a recent inquiry into the "mechanism" of the Volhard reaction (Note 18); and it may be added that racemisation has been found to occur when *lævo*-valeric acid is brominated by Volhard's method (Note 19)—a result which must follow if enolisation take place, although susceptible of another explanation.

So far as I can form a judgment, no case has been made out for the view that substitution of halogen for hydrogen under Volhard's conditions differs in its "mechanism" from substitution in the paraffins. This opinion finds support in the discovery just announced by Leuchs (Note 20) that, while the chief product of the bromination of *dextro*-β-carboxybenzyl-α-hydrindone—

$$C_6H_4 < \begin{matrix} CH_2 \\ CO \end{matrix} > CH \cdot CH_2 \cdot C_6H_4 \cdot CO_2H \rightarrow$$
$$C_6H_4 < \begin{matrix} CH_2 \\ CO \end{matrix} > CBr \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$$

is the racemic compound, no less than 10 per cent is the *dextro*-bromo-derivative ; therefore, the inference is clear that in the formation of the latter compound, if not of both, substitution was effected by a process in which migration of the hydrogen atom did not occur.

Attention may now be directed to the question of "direct substitution," which, in its simplest form, is encountered in the paraffin series. As will be gathered from the following selection from among the various theories propounded to account for the mechanism of substitution, alternative explanations of the intermediate reactions leading up to substitution in these cases involve either elimination of the hydrogen atom before introduction of the halogen, or addition of the halogen in virtue of the supposed residual valency of both molecules, followed by disruption of the complex thus formed into the known products of the change.

Dealing with these alternatives in the order given, Arrhenius adopts a view of the process of substitution, which, including as it does his explanation of optical inversion and racemisation, should perhaps be given in his own words :—

"Every valency linking can be broken ; this is true in all cases, since it is a necessary condition for every chemical reaction. An atom or an atomic complex is thereby removed from the molecule, and its place taken by another atom or atomic complex. One must therefore assume, as was first pointed out by Williamson, that the atoms or complexes separate themselves from the molecule from time to time, even when they do not react with other molecules. Consider now a molecule in which four different atoms, A, B, C, and D, are bound to one carbon atom. The atoms A and B, which may possess equal charges, *e.g.*, positive, are therefore separated at times from the molecule, and it may happen that they are both separated at one and the same time. It is therefore possible for them to change places on combining with the carbon atom again. This is synonymous with a transformation of the original molecule into its optical isomer (Note 21).

Nef, making use of "the conception of dissociation in its broadest sense," is of opinion that the decomposition of ethane into hydrogen and ethylene at 800° "proves that an extremely small per cent of [its] molecules must exist at ordinary temperature in an active or dissociated condition,—

$$CH_3 \cdot CH_3 \rightarrow CH_3 \cdot CH_2 + H -$$" (Note 22),

consequently, when "chlorine reacts with ethane to give the monochloro- substitution product, we have this reagent in the *active molecular* condition simply uniting by addition with the dissociated ethane particles,—

$$\begin{matrix} Cl = Cl \\ | \quad | \\ | \quad | \end{matrix} + H - C_2H_5 \rightarrow \begin{matrix} Cl = Cl \\ | \quad | \\ H \quad C_2H_5 \end{matrix} \quad [\rightarrow HCl + C_2H_5Cl.]$$"

Finally, he draws the conclusion that "excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an additive compound."

Michael (Note 23), in many published papers, has emphasised the view that in the substitution of halogen for hydrogen in a saturated hydrocarbon or saturated acid the principal factors to be taken into account are the mutual chemical attraction of the two elements, on the one hand, and that of the halogen and carbon, on the other. By applying his "positive-negative" hypothesis to the directing influence of "relatively-positive" methyl, and

"relatively-negative" carboxyl, he draws conclusions about the degree of firmness or looseness with which particular hydrogen atoms are bound to carbon in the molecule, and is thereby able to forecast with some success the position or positions in which replacement of hydrogen by halogen will occur. Flürscheim, in the discussion of the relation between the strength of acids and bases, and the quantitative distribution of affinity in the molecule, also makes use of the idea that the relative degree of firmness or looseness with which a hydrogen atom is held depends on the nature of the other atoms or radicals associated with the same carbon atom (Note 24). The hydrogen atoms therefore are not to be regarded as retained in the molecule with the same degree of firmness; in other words, valency is not a constant to be measured in units.

It will be gathered, therefore, that Arrhenius and Nef, from different standpoints, support the idea that separation of hydrogen from the hydrocarbon precedes entry of the substituent into the molecule; Michael and Flürscheim are concerned chiefly with the distribution of valency in the molecule, which determines whether a particular hydrogen atom shall be displaced by hydrogen or not; Kekulé's hypothesis requires addition to precede substitution. Is there any experimental evidence to indicate where the balance of probability lies? I think it can be argued that the phenomena of substitution observed with optically active substances do not lend support to the views of Arrhenius or of Nef, which imply actual or virtual dissociation, but that they point to the intermediate formation of an additive product, which undergoes scission as Kekulé supposed. Such an additive product can be formed only if residual valencies be present in both carbon compound and addendum.

The argument runs thus:—Unless valency has fixed direction in space, a conception now abandoned if modern theories of valency be accepted, the conclusion seems to be inevitable that dissociation of the optically active compound—

$$CWXYZ \text{ into } \dot{C}WXY + Z,$$

must lead to racemisation, the radicals W, X, Y, distributing themselves in two-dimensional space, thus destroying the asymmetry; whence it follows that introduction of the substituent, V, into the molecule in place of Z can give rise only to an optically inactive product. Now, it is a well established fact that a radical attached directly to the asymmetric carbon atom may be replaced by another without racemisation following (Note 25). Therefore, preliminary dissociation being excluded, Kekulé's additive hypothesis remains. But the prolonged study of that remarkable reaction known as the "Walden inversion" by Emil Fischer, McKenzie, and other investigators has led to results which, if the views formed independently by Fischer (Note 26), Werner (Note 27), and Pfeiffer (Note 28) may be accepted, are inexplicable unless a preliminary addition, effected as it is supposed by means of residual valencies, precedes this replacement of the eliminated radical by the substituent.

The Walden inversion may be illustrated by a brief statement of some of the facts discovered in connection with the conversion of optically active chlorosuccinic acid into malic acid

$$R{\cdot}CH(OH){\cdot}CO_2H \rightarrow R{\cdot}CHCl{\cdot}CO_2H \rightarrow R{\cdot}CH(OH){\cdot}CO_2H.$$

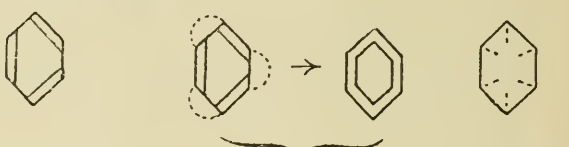
Walden found that *lævo*-chlorosuccinic acid, obtained from *dextro*-malic acid, furnished either *dextro*- or *lævo*-malic acid, according to the reagent used to effect of the replacement of the Cl by the OH radical.

$$l\text{-Chlorosuccinic acid} \begin{cases} \rightarrow (+Ag_2O) \rightarrow l\text{-malic acid.} \\ \rightarrow (+KOH) \rightarrow d\text{-malic acid.} \end{cases}$$

And as the corresponding inversion was found to occur with *dextro* chlorosuccinic acid under similar conditions, a complete cycle of changes can be brought about (Note 29). That preservation of optical activity, and not racemisation, should accompany the replacement of a radical, attached to the asymmetric carbon atom, by another is a fact of much theoretical interest, as has already been indicated; that a change in the sign of rotation should occur when an exchange of the same radicals is achieved by one reagent and not by another is a mystery, that deepens rather than diminishes with each addition to the list of inversions, already long, in which it has been observed (Note 30). In all probability the discovery of the Walden inversion, as Prof. Frankland has said, "may mark an epoch in our views with regard to the mechanism of the process of substitution in general" (Note 31).

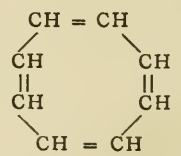
The Structure of the Benzene Molecule.

The abandonment of the theory of the fixed valency unit in favour of the view that the carbon atom has both principal and residual valencies has raised afresh that perennial topic of controversy—the structure of the benzene molecule. Probably few will contest the statement that for practical purposes only three formulæ have emerged from the long discussion of the problem, viz., Kekulé's oscillation formula with fixed valency units, for which much physical evidence has been pleaded; Thiele's formula, in which his theory of "conjugated double linkings" is applied to the Kekulé formula, with the consequence that the three double linkings disappear owing to self-neutralisation of the partial valencies, the benzene molecule thus containing six inactive double linkings (Note 32); and Armstrong's "centric" formula, in which by its residual valency "each individual carbon atom exercises an influence upon each and every other carbon atom" (Note 33). The dotted lines indicate he residual valencies.



Kekulé. Thiele. Armstrong.

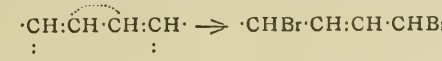
The discovery of *cyclo*octatetraene has brought a new interest into the discussion (Note 34), for the structural formula assigned to this hydrocarbon shows alternate single and double linkings as in Kekulé's symbol, and the optical behaviour (refractivity) corresponds with that of benzene.



But its chemical properties are entirely different from those of benzene; it forms compounds not by substitution but by addition, and it has the reactivities of a highly unsaturated compound. If these experimental results be accepted, then—as Willstätter shows—the peculiar properties of benzene are not to be explained by Kekulé's or Thiele's formula, and the verdict is given in favour of the "centric" symbol—that earliest embodiment of the conception of residual valency, which Armstrong later turned to such good account in the quinonoid theory of colour identified with his name.

The reference to the optical behaviour of *cyclo*octatetraene may perhaps suggest the inquiry:—Do not the physical properties of the carbon compounds throw light on the questions that have been raised? A little consideration will show that, on the contrary, the answer must be:—It is only by chemical evidence that physical data can be interpreted or corroborated, and in the absence of such evidence the "additive" results which accrue from

physical observations have no bearing on questions involving the determination of structure or the structural transformations which accompany a chemical change. For example, the anomalous results obtained by Brühl and by Sir William Perkin (Note 35) in the investigation of the refractivity and the magnetic rotation of certain unsaturated compounds, remained without explanation until Thiele in 1899, by his hypothesis of partial valency, accounted for the comparative inactivity of the central pair of carbon atoms in compounds of this type—compounds which are characterised by containing alternate single and double linkings in their formulæ



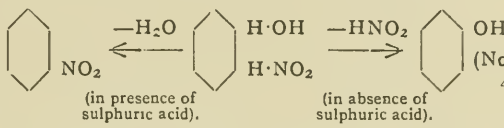
This conception of Thiele's has both focussed attention on the distribution of valency within the molecule, contributing largely to the wide acceptance of theories of valency such as Werner's, and given to the study of physical properties—especially those "constitutive" properties of refraction, dispersion, and magnetic rotation—an impetus which has by no means spent its force. Further, the occurrence of this anomaly, "exaltation" as it is called, is now relied on as evidence of the presence of this particular distribution of valency, with results which in Auwers's hands have furnished important clues to the structural formulæ of terpenes and other compounds.

As additive properties become constitutive, so the value of a knowledge of the physical properties of a substance will tend to increase, but there is little ground for hope that the problem of the constitution of benzene will be solved from the physical side. The controversy which has arisen between Hantzsch and Auwers regarding the physical properties of *cyclo*octatetraene in relation to its chemical structure is a case in point (Note 36); the absence of optical exaltation in this hydrocarbon is wholly unexpected; but, on the other hand, the type of compound is entirely new. With benzene also the distribution of valency within the molecule differs from that in any known compound; our knowledge of it, admittedly far from complete, has been gained from the chemical side, and is summarised in the various structural formulæ; but the limitations of the physical method of attack can be traced from Thomsen's endeavour to determine its structure from thermochemical data (Note 37) to the more recent invention of isorropesis. And, despite the evidence obtained from refractivities, we may not unreasonably demur to the suggestion that derivatives of benzene, which by their behaviour towards substituting agents show themselves to be wide apart in chemical properties, such as nitrobenzene and aniline on the one hand or chlorobenzene and phenol on the other, should respectively be classified together (Note 38). Undoubtedly, most useful information is obtained from a comparison of the physical properties of two related substances, the exact constitution of one of which is uncertain, but that of the other known. Therefore, bearing in mind the great development that has taken place recently in the correlation of physical properties with chemical constitution by methods based on refraction and absorption, every chemist will welcome the entry of Dr. Lowry into that field of research on the relation between magnetic rotation and structure, which for all time will be associated with Sir William Perkin's name.

Substitution in the Benzene Series.

Turning now to a discussion of the problem of substitution in cyclic compounds, one important factor must not be overlooked; the even distribution of the residual affinity of the benzene molecule is disturbed by the introduction of a substituent. The study of substitution in benzene derivatives indicates that, as a consequence of this disturbance, a directing influence comes into play which, when the substituent is changed, may vary in the effect it exercises on the course of substitution.

Arising probably from this even distribution of valency it is characteristic of benzene to furnish additive compounds in which six atoms of hydrogen or a halogen, but not two or four, become attached symmetrically to the molecule; substitution, however, occurs when a catalyser is present, such as the aluminium mercury couple for halogenation, or sulphuric acid for nitration or sulphonation, leading initially to the production of mono-substituted derivatives. Whether the catalyser by association with the benzene molecule (Note 39) limits this additive capacity, or whether its function is to promote the elimination of the halogen acid or water respectively (Note 40), is still a subject of discussion, but in the absence of a reaction of additive type it is not easy to account for facts such as the production of a certain amount of trinitrophenol when benzene is nitrated in the absence of sulphuric acid.



The much-debated questions still remain: Why and by what mechanism, when a second or third substituent is introduced into the molecule, is the orientation of the isomeric products determined by the radical or radicals already present? For disubstitution, the *ortho-para*- and the *meta*-laws have been deduced, and the radicals which respectively promote mainly *ortho-para* substitution on the one hand and *meta*-substitution on the other have been catalogued (Note 42). But these laws take account only of the orientation of the chief product or products, whereas all three derivatives, *ortho*, *meta*, and *para*, have been detected in most of the reactions studied, and their relative proportion in many cases is known to depend on the conditions, being affected by such influence as variations in temperature or in the medium employed (Note 43). Nitration of acetanilide, for example, furnishes a mixture of *ortho*- and *para*-nitracetanilide, but of aniline in the presence of much sulphuric acid yields chiefly *meta*-nitraniline (Note 43). And, to illustrate the inadequacy of the *meta* law, the fact that sulphonation of benzenesulphonic acid with concentrated sulphuric acid at 230—240° furnishes an equilibrium mixture of the *meta*- and *para*-disulphonic acids in the proportion of 2 : 1 may be quoted (Note 44).

In the exploration of this field many workers have participated, but the results, recorded almost as often in patent specifications as in journals, are seldom quantitative, so great is the difficulty at times in isolating the minor product or products of the change. Recently, however, by a most ingenious use of melting-point curves and density determinations, Holleman and his colloborators have carried out an exhaustive series of substitutions with small quantities of material and under known conditions (Note 45); yet after a survey of the whole field the conclusions reached are:—

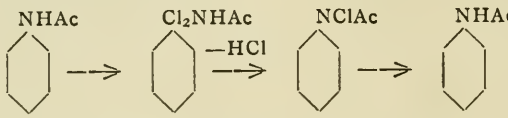
1. That uncertainty cannot be removed until some basis exists for different reactions to be carried out under comparable conditions (Note 46).

2. That even if the relative amounts of the isomerides formed when a radical C is introduced into each of the mono-substitution derivatives $C_6H_5 \cdot A$ and $C_6H_5 \cdot B$ be known, it is not possible to calculate the proportion in which the isomerides $C_6H_3 \cdot ABC$ will be produced when the radical C is substituted in the compound $C_6H_4 \cdot AB$.

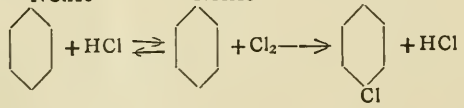
Although the validity of the *ortho-para*- and of the *meta*-laws may be impeached, they serve as a first approximation, and many theories have been propounded to account for them. Armstrong has suggested that in *ortho-para*-substitution the additive compound is formed by association of the addendum with the carbon atom carrying the radical already substituted in the molecule (Note 47), whereas in *meta*-substitution it arises by union of the addendum with this radical (Note 48), transformation to the respective disubstitution derivatives being effected

possibly in step-by-step progression, as conjectured by Lapworth (Note 49). Holleman, who also adopts the additive hypothesis, is of the opinion that the radical already present in the molecule may promote or retard the association of the addendum with the pair of carbon atoms, to one of which it is itself attached. By the operation of the first of the alternatives an *ortho-* and by conjugation a *para*-derivative will arise; from the second a *meta*-derivative will result, when scission of the additive compound ensues. Holleman's is the only hypothesis which has been submitted to the test of quantitative investigation, and although, as already mentioned, the results do not suggest that finality has been reached, it marks an advance in the study of this obscure problem (Note 50).

No discussion of substitution in the benzene series would be adequate without reference to the remarkable behaviour of amines and phenols. Unlike other mono-substitution derivatives, which do not differ markedly from benzene in reactivity, these furnish mono-, di-, and tri-derivatives very readily. With aniline or acetanilide, substitution occurs first of all in the side-chain, being followed under appropriate conditions by removal of the substituent from the amino-group and entry into positions relatively *ortho-*, *para*, or both *ortho-* and *para* to it. The earliest of these changes to be studied was the transformation of methyl-aniline into *para*-toluidines; many of them have been discovered by Chattaway and his collaborators, and until a critical study of the chlorination of acetanilide was undertaken by Orton and Jones (Note 51), it was held that the changes, which occur only in the presence of hydrochloric acid, were of the type :—

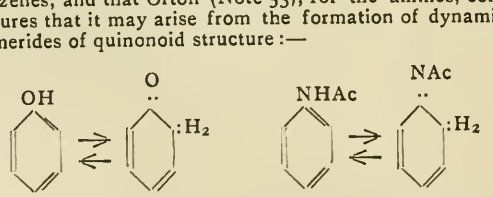


From the dynamics of the reaction, it is now known that intra-molecular transformation from the side-chain to the ring does not occur, the agent promoting the substitution being chlorine arising from the following series of reactions :—



As bromination has been shown to follow the same course, it is evident that no secure foundation now exists for the view, formerly widely held, that the reactivity of amines is intimately connected with the variable valency of nitrogen leading to initial substitution in the side-chain.

Even were this view, now discredited, still applicable to the amines, it could not be extended with the same certainty to the phenols. Hence, in explanation of the rigid adherence to the *ortho para-* law observed among the mono- substitution derivatives of these two groups of compounds, it is noteworthy that Thiele (Note 52), for the phenols, suggests that the reactivity may be due to these substances being stable enolic forms of ketodihydrobenzenes, and that Orton (Note 53), for the amines, conjectures that it may arise from the formation of dynamic isomerides of quinonoid structure :—



How far these suggestions may open up a new field of inquiry into the "mechanism" of substitution remains to be seen; it is at least interesting that their extension to the naphthalene series shows that not only does the reactivity of the naphthols and of α-naphthylamine recall that of phenol and aniline, but the orientation of their mono- substitution derivatives (Note 54) in almost every case is the same as that of one or other of the six naphthaquinones, the existence of which has been predicted by Willstätter (Note 55).

Notes.

1. These schools in 1881 became the Normal School of Science, and in 1900 the Royal College of Science, now incorporated in the Imperial College of Science and Technology.

2. J. N. Collie and H. S. Patterson, *Trans. Chem Soc.*, 1913, ciii., 419; *Proc. Chem. Soc.*, 1913, xxix., 217.

3. Sir J. J. Thomson, *Proc. Roy. Soc.*, 1913, lxxxix., A, 20.

4. A. Claus, *Ber.*, 1881, xiv., 435. It may be noted that Claus concludes his paper with the statement, " . . . die Annahme von Valenzen als in den mehrwerthigen Atomen präexistirender ihrer Wirkungsgrösse nach bestimmter Anziehungseinheiten eine ebenso unbegründete, wie unnatürliche Hypothese ist."

5. A. Werner, " Neuere Anschauungen auf dem Gebiete der anorganisehen Chemie " (Friedr. Vieweg u. Sohn, Braunschweig, 1908); English edition, " New Ideas on Inorganic Chemistry," E. P. Hedley. (Longmans, 1911).

6. A. Werner, *Ber.*, 1911, xliv., 2445, 3231.

7. S. U. Pickering, *Proc. Chem. Soc.*, 1885, i., 122; H. E. Armstrong, *Proc. Roy. Soc.*, 1886, xl., 285.

8. As an example of the unsatisfactory character of the doubly linked formula to which the older meaning was attached, the following may be quoted :—*unsym.*-Diphenyl-dichloroethylene, like ethylene, combines molecularly with bromine, but tetraphenylethylene does not.—

CH_2	$C(C_6H_5)_2$	$C(C_6H_5)_2$
||	||	||
CH_2	$C\,Cl_2$	$C(C_6H_5)_2$

yet a similar structure has been assigned to each (Biltz, *Annalen*, 1897, ccxcvi., 219).

9. P. F. Frankland, *Proc. Chem. Soc.*, 1913, xxix., 101.

10. J. Volhard, *Annalen*, 1887, ccxlii., 141; *Ber.*, 1888, xxi., 1904.

11. L. Van Raymenant, *Bull. Acad. Roy. Belg.*, 1900, p. 724. For the chloroketobutanes, *cf. Idem.*; Kling, *Comptes Rendus*, 1905, cxl., 312; *Bull. Soc. Chim.*, 1905, [3], xxxiii., 322.

12. A. Michael, *Ber.*, 1901, xxxiv., 4035, 4046.

13. C. Montemartini, *Gazz. Chim. ital.*, 1897, xxvii., [2], 368; 1898, xxviii., [2], 290).

14. It may be of interest to note that the long controversy respecting the composition of ordinary ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OEt$, the first of these desmotropic compounds to be discovered, has been brought to an end by the isolation of each desmotropic form at temperatures sufficiently low to inhibit the desmotropic change. From refractometric observations with mixtures of the pure isomerides, Knorr concludes that this ester at the ordinary temperature contains about 2 per cent of the enolic form, whereas from bromination experiments with the etser itself, which may possibly be accompanied by a disturbance of the equilibrium, K. H. Meyer infers that the amount may be as much as 7 per cent. (L. Knorr, O. Rothe, and H. Averbeck, *Ber.*, 1911, xliv., 1138; K. H. Meyer, *Annalen*, 1911, ccclxxx., 222; K. H. Meyer and P. Kappelmeier, *Ber.*, 1911, xliv., 2718).

15. A. Lapworth, *Trans. Chem. Soc.*, 1904, lxxxv., 31; H. M. Dawson with May S. Leslie, *Ibid.*, 1909, xcv., 1860; with R. Wheatley, *Ibid.*, 1910, xcvii., 2048: with F. Powis, *Ibid.*, 1912, ci., 1503.

16. K. H. Meyer, *Ber.*, 1912, xlv., 2867.

17. O. Aschan, *Ber.*, 1912, xlv., 1913; 1913, xlvi., 2162; K. H. Meyer, *Ber.*, 1912, xlv., 2868.

18. J. Volhard, *loc. cit.*

19. O. Schütz and W. Marckwald, *Ber.*, 1896, xxix., 58.
20. H. Leuchs, *Ber.*, 1913, xlvi., 2435.
21. S. Arrhenius, "Theories of Chemistry," edited by T. Slater Price (Longmans, 1907), p. 76.
22. J. U. Nef, "The Fundamental Conceptions underlying the Chemistry of the Carbon Atom," *Journ. Am. Chem. Soc.*, 1904, xxvi., 1566.
23. A. Michael, *Ber.*, 1901, xxxiv., 4028, covering reference to earlier papers.
24. B. Flürscheim, *Trans. Chem. Soc.*, 1909, xcv., 721.
25. P. Walden, *Ber.*, 1895, xxviii., 1297; W. A. Tilden and B. M. C. Marshall, *Trans. Chem. Soc.*, 1895, lxvii., 494.
26. E. Fischer, *Annalen*, 1911, cccIxxxi., 123.
27. A. Werner, *Ber.*, 1911, xliv., 873.
28. P. Pfeiffer, *Annalen*, 1911, cccIxxxiii., 123.
29. P. Walden, *Ber.*, 1896, xxix., 133; 1897, xxx., 3146; 1899, xxxii., 1833, 1855.
30. Without the aid of a model it is not possible to show that the production of the *dextro-* or *lævo*-acid may be accounted for by the hypothesis that an intermediate additive compound is formed, which undergoes scission in one or other of two ways. Diagrams of models will be found in Fischer's paper (*loc. cit.*, *cf.*, *Annual Reports on the Progress of Chemistry* (Gurney and Jackson), 1911, viii., 67), and to illustrate Werner's hypothesis, which is more explicit than Fischer's, in a paper by W. E. Garner (*Proc. Chem. Soc.*, 1913, xxix., 200).
31. P. F. Frankland, "The Walden Inversion," Presidential Address to the Chemical Society (*Trans. Chem. Soc.*, 1913, ciii., 713).
32. J. Theile, *Annalen*, 1899, cccvi., 126.
33. H. E. Armstrong, *Trans. Chem. Soc.*, 1897, li., 264 (footnote).
34. R. Willstätter and E. Wasser, *Ber.*, 1911, xliv., 3423.
35. *Cf.*, J. W. Brühl, *Ber.*, 1907, xl., 878; Sir W. H. Perkin, *Trans. Chem. Soc.*, 1907, xci., 806, for references to earlier papers.
36. A. Hantzsch, *Ber.*, 1912, xlv., 563; K. Auwers, *Ibid.*, 971.
37. *Cf.*, H. E. Armstrong, *Phil. Mag.*, 1887, [5], xxiii., 73; J. W. Brühl, *Journ. Prakt. Chem.*, 1887, [2], xxxv., 181, 209.
38. *Cf.*, J. W. Brühl, *Zeit. Phys. Chem.*, 1894, xvi., 220; Smiles, "Relations between Chemical Constitution and Physical Properties" (Longmans, 1910), p. 299.
39. B. N. Menschutkin, Abstr. *Chem. Soc.*, 1912, cii., [1], 98—100.
40. *Cf.* H. E. Armstrong, *Trans. Chem. Soc.*, 1887, li., 263.
41. The phenyl by nitration forming the trinitro derivative (picric acid), Armstrong and Rossiter, also Groves, *Proc. Chem. Soc.*, 1891, vii., 89.
42. *Cf.* Noelting, *Ber.*, 1876, ix., 1797; Armstrong, *Trans. Chem. Soc.*, 1887, li., 258; Crum Brown and Gibson, *Ibid.*, 1892, lxi., 367.
43. Hübner, *Annalen*, 1881, ccviii., 299.
44. J. J. Polak, *Rec. Trav. Chim.*, 1910, [ii.], xiv., 416; R. Behrend and M. Mertelsmann, *Annalen*, 1911, cccIxxviii., 352.
45. A. F. Holleman, "Die Direkte Einführung von Substituenten in den Benzolkern" (Leipzig, Viet and Co., 1910), p. 215.
46. For example, nitration is effected chiefly at low temperatures, but sulphonation of mono-substituted benzenes at temperatures higher than the ordinary, which if employed in nitration would lead to mixed products.
47. Kinetic studies of the chlorination and bromination of toluene, $C_6H_5 \cdot CH_3$, however, gave no indication of the production of an intermediate additive compound of the hydrocarbon and addendum (*cf.* Holleman, Polak, van der Laan, and Euwes, *Rec. Trav. Chim.*, 1908, xxvii., 435; Brunner and Dluska, *Bull. Acad. Sci.*, Cracow, 1907, p. 693; Bancroft, *Journ. Phys. Chem.*, 1908, xii., 417; Cohen, Dawson, Blockey, and Woodmansey, *Trans. Chem. Soc.*, 1910, xcvii., 1623).
48. H. E. Armstrong, *Trans. Chem. Soc.*, 1887, li., 258.
49. A. Lapworth, *Trans. Chem. Soc.*, 1898, lxxiii., 454; 1901, lxxix., 1265.
50. It should be mentioned that other views, based on the loosening or strengthening of the affinity of the hydrogen atoms situated in *ortho-*, *para-*, or in *meta*-positions, brought about by the disturbing influence of the radical already present in the molecule on the valency of the carbon atom to which it is attached, and therefore on that of the other five carbon atoms, have been advanced by Flürscheim (*Journ. Prakt. Chem.*, 1902, [ii.], lxvi., 321), Tschitschibabin (*Ibid.*, 1912, [ii.], lxxxvi., 397), and others.
51. K. J. P. Orton and W. J. Jones, *Brit. Assoc. Report*, 1910, p. 96; *Trans. Chem. Soc.*, 1909, xcv., 1456.
52. J. Thiele, *Annalen*, 1899, cccvi., 129.
53. British Association Report, 1910, p. 96.
54. *Cf.*, W. P. Wynne, art. "Naphthalene," Thorpe's *Dictionary of Applied Chemistry*, second edition, vol. iii. (Longmans, 1912).
55. R. Willstätter and J. Parnas, *Ber.*, 1907, xl., 1406.

(To be continued)

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Parachutes for Aeroplanes.

The audacious experiment of the aviator Pégond, who at a height of 300 metres left his aeroplane to descend to the ground by the help of a parachute, has brought to the front the interesting question of parachutes for aeroplanes. It was only about the year 1910 that the idea of employing parachutes for assuring the safety of aviators was considered for the first time. Until then security was sought for only in the qualities inherent to the machine, any additional apparatus being considered inefficacious, if not dangerous. The problem of the use of parachutes is, indeed, a very particular one, for these apparatus must be ready to act whatever may be the position, speed, and height of the avion to which they are attached. That is the real difficulty of the problem, a difficulty that a large number of inventors seem to ignore systematically. Ordinary experiments, in which the parachute is, at the start, placed in a convenient position, animated by a very slow speed, sometimes even with no speed at all, being far removed from the real conditions in which the apparatus has to work in all positions and at speeds of more then 100 kilometres an hour, and especially instantaneously in order that its efficacy may be immediate. Lastly, it must be remembered that to descend a weight of 75 kilogrms. at a speed of 4 or 5 metres per second the surface of the parachute must have a development of 60 square metres. It is, then, the complete condemnation of parachute garments, of which the most sadly celebrated were those of Reicheld, which caused the death of their inventor during an experiment at the Eiffel Tower. That is also the reason of the repeated failures of parachutes of the umbrella system with stiff frames, the development of which is very uncertain. The only apparatus that, up till now, have given good results are the supple parachutes, of which the principal ones are those of Hervieux, Cremoux, Dangy-Baillet, Bonnet, and Ochs. What characterises them all is the special arrangement enabling their instantaneous development, which is, indeed, the essential condition required. In the Hervieux parachute, the prototype of the kind, the buffer springs are placed all along the periphery of the parachute, which is enclosed in a case, and the springs are then strongly compressed. When a little spring is pressed the box opens, and the springs of the parachute shoot out violently, thus determining the immediate development of the silk of the parachute. In the Dangy-Baillet, Crémoux,

and Bonnet parachutes it is a buffer filled with air, running along the whole or part of the periphery that produces the opening of the machine. In the Ochs system it is steel springs that do the work.

The Struggle against Tuberculosis.

Recently at the Academy of Sciences, M. Chauveau spoke of one of the means advised for fighting against tuberculosis—obligatory declaration. The advantages to be drawn from this declaration are perhaps somewhat illusory. Of what use will it be? Of none; for it is impossible to fight against the propagation of the germs. And then, again, says he, the germ is nothing after all; it is the ground that is everything. We live in an environment infected with myriads of tuberculous germs and yet we are not all tuberculous. Only weakened organisms are affected, healthy organisms are refractory. M. Chauveau next calls attention to a long and costly experiment that he made concerning the virulence of tuberculosis, on a lot of 60 oxen that he had to feed for a long period before having them successively slaughtered. He likewise recalls an experiment of clavelous contamination of which he is the author.

Study of Rolling of Ships.

M. Bertin, Chief Engineer for Naval Ship Building, when presenting, before the Academy of Sciences a work of M. Bogaert, a Belgian engineer, on the gyroscopic effect, especially brought to notice the study made in this work of the old pegged oscillograph, which was the first instrument employed to measure rolling. On this occasion he retraces the history of the double oscillograph which he employed for his observation on swell and rolling. The first instrument, a simple trial model, dates from 1868; it was supplied with two pendulums, one of long, the other of short period. The first pendulum could not reach the duration required, and that led M. Bertin to propose the combination of the gyroscope and the short pendulum which has never yet been realised. In 1871, in England, Mr. William Froude constructed an oscillograph with two pendulums, one of which was a large pendulum of a suit able period. From this example, the following year M. Bertin had an apparatus eonstructed conformable to his first idea, and which has given good results.

The Individuality of Protozoa.

The question has often been discussed to know if the protozoa, which frequently divide into two, keep or lose their individuality after this division. If, indeed, they kept it they would be immortal, since they can keep on dividing themselves indefinitely when they are in a suitable environment. Weissman had also affirmed their immortality, that he opposed to the precarious duration of the bodies of higher animals. But this immortality does not appear to exist according to the latest experiments of Metchnikoff, who fed Paramesies with carmine grains. They at first swallow a great quantity, but after a few days they learnt to refuse them, and no longer swallow a single grain. Now if at this moment the Paramesie divides the individual daughters have lost all remembrance of the former experiments and again absorb the carmine. The protozoa that divides itself seems to cease to live as an individual and to give birth to two individuals, completely new; it is, then, not immortal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 26, June 30, 1913.

Preparation of Diphenylpentanes and the Corresponding Dicyclohexylpentanes.—Paul Sabatier and M. Murat.—By direct hydrogenation over nickel of the corresponding acids the authors have prepared three of the eighteen possible diphenyl hydrocarbons derived from pentane or its isomers, viz., 1·5-diphenyl pentane from normal pentane and two from methyl-2-butane. When subjected to direct hydrogenation over nickel they are all converted into the corresponding dicyclohexylic hydrocarbons. It is noticeable that all the diphenyl hydrocarbons are fluorescent, especially those of normal structure which possess a formic chain with a phenyl group at each end. The dicyclohexylic compounds are not fluorescent.

Hydrates of Uranic Anhydride and Heat of Formation of Uranyl Nitrate.—M. de Forcrand.—Uranic acid, $UO_3.H_2O$, is a fairly stable hydrate which boils at about 220° C. The dihydrate boils at 135° and effloresces rapidly at 80°. It loses a molecule of water (slowly) over sulphuric acid. The heat of formation of $N_2O_6UO_2$(solid) from UO_2 (sol.) O_6 (gas) and N_2 (gas), is +67·25 cal., and of $N_2O_6UO_2$ (dissolved) + 86·25 cal. These values approach those given by copper.

Chemical Lability and Absorption of Ultra-violet Rays.—Victor Henri.—According to the electronic theory of chemical reactions a substance which reacts easily contains molecules which can easily liberate or exchange electrons, and the bonds between the atoms in the molecules are produced by electrons. The absorption of ultra-violet rays being an electronic property it might be supposed that there is a connection between the absorption and the lability of substances. This conjecture is confirmed by the study of series of substances belonging to the same chemical families, some being stable and the similar ones labile. It is observed that substances the molecules of which are labile strongly absorb the ultra-violet rays.

Action of CO_2 on Mineral Sulphides. – N. D. Costeanu.—CO_2 has no action on the sulphides of silver, copper, cadmium, bismuth, and antimony when they are heated in an electrical resistance furnace and exposed to its action. With sulphide of silicon it gives silica, carbon monoxide, and sulphur, $2CO_2 + SiS_2 = 2CO + 2S + SiO_2$.

Composition of Gaseous Mixtures resulting from the Action of Water on Carbides of Uranium and Thorium.—P. Lebeau and A. Damiens.—When water acts on uranium carbide the gaseous mixture evolved has approximately the same composition when the same specimen is tested twice, but carbides containing graphite give very different results from those which contain no graphite. The former gave roughly 50 per cent of hydrogen, 24 per cent of ethane, and 13 per cent of methane, while the gases from non-graphitic specimens contain less free hydrogen and more methane, propane, butane, &c.

Azoic Colouring Matters from Phenylisoxazolone.—André Meyer.—The author has prepared various dyes, both acid and substantive, from phenylisoxazolone, *e.g.*, benzene *p*-sulphonate of sodium-azophenylisoxazolone, in order to compare their tinctorial properties with those of the pyrazol dyes. The colours they produce are very often very similar to those produced by the corresponding derivative of pyrazol, but they exhibit much less resistance to the action of light.

Composition of Water Gas.—Leo Vignon.—Water gas consists essentially of nearly equal volumes of carbon monoxide and hydrogen. It also contains carbon dioxide, and the author has proved that a small proportion of methane is always present. It is formed by the following reactions:—

$$4CO + 2H_2O = 3CO_2 + CH_4$$
$$2CO + 2H_2 = CO_2 + CH_4$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

Existence of Bromites.—J. Clarens.—When a solution of hypobromite is raised to about 80° and then treated with an excess of ammoniacal salt it contains a compound which reacts in the cold on arsenious acid but has no action on ammoniacal salt. It is thus neither bromate nor hypobromite, but is probably bromite of formula BrO_2M.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2809.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Birmingham, 1913.

By Prof. W. P. WYNNE, D.Sc., F.R.S., President of the Section.

(Concluded from p. 149).

Symmetric and Asymmetric Syntheses.

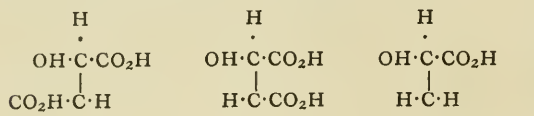
It must not be supposed that the "mechanism" of substitution can be explained by reference only to the examples of this type of reaction which have been mentioned, or that the summary attempted in the restricted field of the replacement of hydrogen by halogen is a complete picture of all the different views advanced to account for this chemical change. Rather, the effort has been made to indicate in broad outline the difficulties that beset any exploration of that debateable region which lies between the two sides of a chemical equation. But, as the wonderful story of carbon chemistry shows, the failure to comprehend the processes operative in substitution does not impede rapid progress in other directions. The study of the mobility of radicals, desmotropy being only one of many examples of this phenomenon, continues to present fresh problems, of which that raised by Thorpe (Note 56) in connection with the mobile hydrogen atom of glutaconic and aconitic acids may be mentioned, as it revives a question of old standing: Do free units of valency exist in carbon compounds? The syntheses of caffeine and certain alkaloids, of sugars and peptone-like polypeptides, of natural terpenes and camphor, of indigo and rubber, are well-known achievements, while natural processes, in which enzyme action plays a part, are yielding their closely guarded secrets to the persistent inquiry of Armstrong and his collaborators, who are probing the relationship between enzyme and substrate which Emil Fischer pictured as that of lock and key. Further, there is that large field of work which includes not only the Walden inversion but new problems of asymmetry, with which the names of Frankland, Pope, Werner, and others are associated; while Barlow and Pope's conception of the relation of valency to atomic volume, by correlating crystalline structure with the composition, constitution, and configuration of carbon compounds, has given a new interest so the study of crystallography.

Nor is progress less rapid in that other important branch of chemistry—the unravelling of the structure of natural products. The constitution of rubber is approximately known; most of the alkaloids have been explored with a greater or less degree of completeness; and now the study of starch (Note 57), chlorophyll, and hæmatin (the non-proteid constituent of hæmoglobin) (Note 58) has been taken up afresh during the last three years, with results which, in the case of the two latter, eclipse in importance and interest all that was previously known. In whatever direction we may look, there is the same evidence that we can take to pieces the most complicated structure which nature has devised, and by the aid of valency conceptions can fit the pieces into a formula which is an epitome of the chemical activities of the molecule. Again, in many cases the resources of our laboratories enable us to build up the structure thus displayed, and to establish the identity of nature's product and our own. Nevertheless, the fact remains that all these syntheses leave untouched and unexplained the profound difference between the conditions we find necessary to achieve our purpose and those by which the plant or animal carries on its work in presence of water and at a temperature differing only slightly from the normal. It is, of course, a well-known fact that an enzyme under the appropriate conditions can bring about the same chemical transformation of a substrate as is effected by the living cell from which it can be separated; but our knowledge of these complex, ill-defined, nitrogenous organic compounds is relatively very meagre; they are difficult to purify, and their composition—apart from any question of structure—is largely unknown. Yet because Wöhler chanced to discover that urea can be produced synthetically from an inorganic source the conclusion is not infrequently drawn that all chemical changes in living substance are brought about by ordinary chemical forces (Note 59). Probably everyone present will concur in that view, but the assent, if given, can hardly arise from a consideration of the facts, of which there is no great store. Where so little is known accurately, chemistry is not on very safe ground if she infer the rest. What common basis of comparison exists between Wöhler's process and the metabolic changes by which urea is produced in the living body? What evidence have we that because an enzyme and an inorganic agent under different conditions give rise to the same end product, the driving force is the same, although the lines along which it is exercised are very different? I think it is not the least of the many services which Prof. Meldola has rendered to chemistry, that he has given us this warning:—"If we have gone so far beyond Nature as to make it appear unimportant whether an organic compound is producible by vital chemistry or not, we are running the risk of blockading whole regions of undiscovered modes of chemical action by falling into the belief that known laboratory methods are the equivalents of unknown vital methods" (Note 60).

I turn now to a no less interesting question than that involved in enzyme reactions, namely, the wide distribution in plants and animals of single asymmetric substances which if synthesised in the laboratory would be produced as inactive mixtures of both asymmetric forms. It has been argued that the occurrence of racemic compounds in nature, although infrequent, is a proof that in the organism, as *in vitro*, they are in all cases the initial products from which, when separated into antipodes, one of the asymmetric compounds is utilised in the life processes and the other left. But whether this be the case, or whether only the one asymmetric form result from the synthesis, Pasteur fimly held the view that the production of single asymmetric compounds or their isolation from the inactive mixture of the two forms is the prerogative of life. Three methods were devised by Pasteur to effect this isolation, and in only one of them are living organisms—yeasts or moulds—employed; but Prof. Japp, in his address to this Section at Bristol in 1898, emphasised the fact, hitherto overlooked, that in the two others, nevertheless, "a guiding power [is exercised by the operator] which is akin in ts results to that of the living organism, and is entirely beyond the reach of the symmetric forces of inorganic nature." Hence, to quote again from his address, "only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can [bring about the isolation of the single asymmetric compound]. Only asymmetry can beget asymmetry." After an exhaustive review of the subject, Japp came to the conclusion that the failure to synthesise single asymmetric compounds without the intervention, either direct or indirect, of life is due to a permanent disability, and although—as was to be expected—this conclusion was challenged (Note 61), the only "asymmetric syntheses" effected since that time have been operations controlled by the chemical association of an optically active substance with the compound undergoing the synthetical change (Note 62).

Recently the problem has assumed a more hopeful character. Ostromisslensky (Note 63) in 1908 made the remarkable discovery that inactive asparagine, which is not racemic but a mixture of the *dextro-* and *lævo-*forms in molecular proportion, gave a separation of one or othe

isomeride when its saturated solution was inoculated by a crystal of glycine—a substance devoid of asymmetry. Now Erlenmeyer claims to have achieved a true asymmetric synthesis by boiling an aqueous solution of inactive asparagine for sixteen hours, when by crystallisation part of the *dextro*-form separated in an almost pure state (Note 64). The theoretical conclusions which led to this investigation are of much interest because they raise afresh the question whether without displacement of the individual radicals, and apart from antipodes, more than one compound can exist, in the molecule of which two carbon atoms are united by a single linking (Note 65). As an illustration, reference may be made to the malic acid series, in which three optically active compounds are known, the *dextro*-acid, the *lævo*-acid, and Aberson's acid (Note 66). In the *lævo*-series the three isomerides obtainable by rotation of one of the carbon atoms with its attached radicals relatively to the other would be—



Lævo-acid, $[\alpha]_D$ −5·8°. (Not isolated). Aberson's acid, $[\alpha]_D$ +9 8°.

With the inactive asparagine it is supposed by Erlenmeyer that prolonged heating in aqueous solution produces a rotation of this type, possibly to an unequal extent or in opposite directions in the *dextro*- and *lævo*-forms, whereby the products being no longer antipodes become separable by ordinary laboratory methods. It is too early yet to say whether, by exclusion of all asymmetric influences, the riddle has been solved, but it is easy to understand with what interest confirmation of Erlenmeyer's results is awaited.

Honours Students and Post-Graduate Scholarships.

In bringing this address to a conclusion, it will not be an innovation if I refer—it shall be only briefly—to the training of those who will carry on and amplify the work which we in this generation have attempted to do. This section stands for the advancement of chemistry which includes, so closely are pure and applied chemistry intertwined, the advancement of chemistry as applied to industry. Once again the cry has been raised in the press (Note 67) that chemists trained in our Universities are of little value in industrial pursuits; they are too academic; they are not worth their wage—little as that often is, whether judged by a labourer's hire or the cost of a university training. It may be so. On the other hand, it is possible the employer obtains all that he pays for, and by paying more would receive in return much more by the inducement offered to more highly trained men to enter the field. Three years' training for the ordinary degree cannot carry a student very far in chemistry, and this preliminary training—for it is little more—is insufficient to equip the young graduate for more than routine work. With the Honours student it is otherwise. He must either enter on his three years' residence at a University with a knowledge which does not fall below the requirements of the Intermediate Examination, and devote the greater part of his time to his Honours subject, or he must be prepared to spend a fourth year to reach the necessary standard. More highly equipped in the academic sense than a man who has worked only for the ordinary degree, he undoubtedly is, yet there is seldom time to begin his training in research methods or in methods of commercial analysis where rapidity rather than extreme accuracy is the object in view.

Two reforms, I venture to think, are needed: the first would avoid early specialisation, which is apt to be disastrous, the second would encourage post-graduate training in directions where the student's inclinations or aptitude may be stimulated and developed. If the Civic Universities, established in virtue of charters drafted mainly on similar lines and inspired by similar aims, could come to some agreement requiring three years' residence, subsequent to the Intermediate, for an Honours degree in chemistry, the first reform would be effected—it is a measure for which a strong case can be made out. If, further, they could see their way to standardise their Ordinances and Regulations for the M.Sc. degree, cease to confer it on Honours graduates of one or more years' seniority in return for payment of a fee, and confine it to graduates - not necessarily Honours graduates—who have carried out an approved piece of research during not less than one academic year, Selection Committees, Boards of Directors, or individual employers would have some clue to the type of man before them. I would go further and suggest that the interchange of Honours graduates between the Civic Universities, or between them and other Universities or Colleges, if it could be arranged, would be of much benefit to the student himself. No University in this country is wealthy enough to attract to its service teachers who are pre-eminent in each branch of chemistry. How great, then, would be the gain to an Honours graduate working for the M.Sc. degree, if, instead of being associated with the same teacher during the whole of his academic career, he could migrate from the place which had trained him to spend part, or the whole, of his time in the laboratory of an Armstrong, a Donnan, a Perkin, or a Ramsay, during that most critical period when he is sorting out his own ideas and learning how to use his fingers and his wits. But whether enforcement of the longer training for the Honours degree be possible; whether a research degree as a step to the Doctorate be desirable or practicable, there can be no doubt that the urgent need of the present time is the provision of scholarships and exhibitions, sufficient in value to secure at least a bare livelihood, for post-graduate work. He who is able to convert Education Committees and private donors to the view that a far better return for the money could be assured if part of the large expenditure on scholarships for matriculated or non-matriculated students were diverted to post-graduate purposes, will have done a service to science and the State the value of which, in my opinion, cannot be overestimated.

Notes.

56. N. Bland and J. F. Thorpe, *Trans. Chem. Soc.*, 1912, ci., 871, 1490.

57. H. Pringsheim and H. Langshans, *Ber.*, 1912, xlv., 2533.

58. For summaries of Willstätter's and Marchlewski's "Researches on Chlorophyll," and of Piloty's on "Hæmatin," *cf. Annual Reports on the Progress of Chemistry* (Gurney and Jackson)), 1911, viii., 144—152; 1212, ix., 165—172.

59. "Quite similar changes can be produced outside the body (*in vitro*) hy the employment of methods of a purely physical and chemical nature. It is true that we are not yet familiar with all the intermediate stages of transformation of the materials which are taken in by the living body into the materials which are given out from it. But since the initial processes and the final results are the same as they would be on the assumption that the changes are brought about in conformity with the known laws of chemistry and physics, we may fairly conclude that all changes in living substance are brought about by ordinary chemical and physical forces."— Sir Edward Schäfer, President's Address at the Dundee Meeting, British Association Report, 1912, p. 9.

60. R. Meldola, "The Chemical Synthesis of Vital Products" (Arnold, 1904), p. 7.

61. F. R. Japp, "Stereochemistry and Vitalism." Presidential Address to Section B (Bristol), British Association Report, 1898, p. 826; *cf.* K. Pearson, *Nature*, 1898, lviii., 495; G. Errara; F. R. Japp, *Ibid.*, p. 616;

Ulpiani and Condelli, *Gazz. Chim. ital.*, 1900, xxx., [i.], 344; Byk, *Ber.*, 1904, xxxvii., 4696; Henle and Haakh, *Ber.*, 1908, xli., 4261; Byk, *Ber.*, 1909, xlii., 141.

62. *Cf.*, *inter alia*, McKenzie, *Trans. Chem. Soc.*, 1905, lxxxvii., 1373.

63. I. von Ostromisslensky, *Ber.*, 1908, xli., 3035.

64. E. Erlenmeyer, *Biochem. Zeit.*, 1913, lii., 439.

65. *Cf.* J. Wislicenus, *Ueber di räumliche Anordnung der Atome in organischen Molekulen* (Leipzig, Hirkel, 1889), 28; K. Auwers and V. Meyer, *Ber.*, 1888, xxi., 791.

66. J. H. Aberson, *Ber.*, 1898, xxxi., 1432; P. Walden, *Ber.*, 1899, xxxii., 2720.

67. *Cf. The Times*, Engineering Suppl., 1913, May 7, 21, 28, June 4, 11, 18.

THE PROGRESSIVE BROMINATION OF TOLUENE.*

By JULIUS B. COHEN and P. K. DUTT.

A. K. MILLER (*Trans.*, 1892, lxi., 1023) studied the action of bromine on ortho- and para-bromotoluene separately and identified the dibromotoluenes formed in each case by oxidising the products to the corresponding benzoic acids and fractionally crystallising the barium salts. His results may be summarised as follows:—Ortho-bromotoluene gave the 2 : 5-dibromo- compound as the principal product together with a smaller quantity of the 2 : 4-derivative; para-bromotoluene gave, as the main product, 3 : 4-derivative and a smaller quantity of the 2 : 4 compound.

In comparing these results with those of chlorination of ortho- and para-chlorotoluenes (Cohen and Dakin, *Trans.*, 1901, lxxix., 1111) considerable discrepancies appear. In the case of chlorination of ortho chlorotoluene the main products were the 2 : 4 and 2 : 3, and a smaller quantity of 2 : 6 derivative, whilst the presence of 2 : 5-compound seemed probable but not certain. In the case of the para-compound, the 2 : 4 is the main product and not 3 : 4, as found by Miller in the case of bromination.

Considering this difference in the orienting effect of the two halogens we thought it desirable to repeat Miller's work and extend it along the same lines as were followed in the case of chlorination.

Incidentally, we examined the mixed monobromotoluenes—the first product of the action of bromine on toluene—to detect any trace of the meta-compound if formed. We also carried our investigation as far as the tribromo- stage.

In the following table the results of bromination and chlorination are given side by side, the principal product being placed first in each case and a trace indicated by brackets:—

Toluene.	Bromination products. Ortho-, para- (meta).	Chlorination products. Ortho-, para-.
Monohalogen Compounds.		
Ortho- compound	2 : 5; 2 : 4	2 : 4; 2 : 3; 2 : 6; (2 : 5)
Para - compound	2 : 4; 3 : 4	2 : 4; 3 : 4
Meta - compound	2 : 5; 3 : 4; (3 : 5)	2 : 5; 3 : 4
Dihalogen Compounds.		
2 : 3	2 : 3 : 6; 2 : 3 : 5	2 : 3 : 4
2 : 4	2 : 4 : 5; (2 : 4 : 6)	2 : 4 : 5; 2 : 3 : 4; (2 : 4 : 6)
2 : 5	2 : 4 : 5; (2 : 3 : 5); (2 : 3 : 6)	2 : 3 : 6; 2 : 4 : 5
2 : 6	2 : 3 : 6	2 : 3 : 6
3 : 4	2 : 4 : 5; (3 : 4 : 5)	2 : 4 : 5
3 : 5	2 : 3 : 5	2 : 3 : 5

Attention is directed to the difference produced by chlorination and bromination of orthohaloid toluenes in the orienting effect, which is most marked in the case of the monohalogen compound and the 2 : 3 and 2 : 5 halogen derivatives.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

A SERIES OF MIXTURES OF NITRO-COMPOUNDS AND AMINES WHICH ARE COLOURED ONLY IN THE LIQUID STATE.*

By C. K. TINKLER, D.Sc.

WHILST engaged in an investigation as to the cause of the colour of certain alkyl iodides of cyclic bases in 1908, it was noticed by the author that in some cases nitro-compounds like these alkyl iodides, when dissolved in fused diphenylamine, gave coloured solutions. In the case of the nitro compounds, however, the colour often disappears on cooling. The investigation in connection with nitro-compounds was not pursued very far at that time, but it has recently been extended.

The most suitable substances for the demonstration of this phenomenon are mixtures of diphenylamine with one of the following nitro-compounds: *o*-, *m*-, and *p*-chlor-nitro-benzene, *m*- and *p*-nitrobenzaldehyde, *p*-brom nitro-benzene, tetra-nitromethane. By enclosing one of these mixtures between two test-tubes placed one inside the other the phenomenon is well demonstrated. Thus, a mixture of diphenylamine and para chlor-nitrobenzene, which is colourless at the ordinary temperature, acquires a reddish yellow colour when held in the hand, and loses this colour when the temperature falls.

A mixture of diphenylamine and *p*-nitro-benzaldehyde shows a deep red colour at 1° above body temperature, returning to the colourless state on cooling. A mixture of diphenylamine and tetranitromethane shows a dark brown, nearly black, coloration, but on cooling in a mixture of ice and salt this colour entirely disappears. On repeating the last experiment several times, however, a permanent green colouring is produced, which is probably due to the decomposition of the nitro-compound. In other cases the mixture undergoes no change on keeping. Thus, a mixture of diphenylamine and *p*-chlor-nitrobenzene prepared five years ago shows the phenomenon as well now as when first prepared.

Attempts to precipitate the coloured substances from solution give interesting results. Thus, by treating a concentrated alcoholic solution of a mixture of diphenylamine and *p*-nitrobenzaldehyde with water a red semi-solid mass is obtained, which, however, on complete solidification, produced by agitation, is perfectly white.

From analogy with compounds of amines and nitro-compounds, such as trinitrobenzene, picryl chloride, &c., prepared by previous investigators, it would appear that the colour of these mixtures under consideration is probably due to the combination of nitro-compound and amine in the liquid state only, and hence various physico-chemical investigations of the fused mixtures were undertaken.

The following results were obtained in this connection:—

1. No evidence was obtained of the separation of a compound in the solid state by cooling a fused mixture.

2. No break was observed in the curve, densities: composition, either in the case of a mixture showing the phenomenon, or in the case of a mixture of trinitrobenzene and diphenylamine where a compound exists in the solid state.

3. A very slight rise of temperature was observed when the fused constituents were mixed.

4. No direct evidence of the formation of a compound was obtained by the determination of the viscosity: composition curve for one of the mixtures showing the phenomenon.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

THE INFLUENCE OF CHEMICAL CONSTITUTION ON THE THERMAL PROPERTIES OF BINARY MIXTURES.*

By ERNEST VANSTONE.

BINARY mixtures of compounds of the type Ph *a* *β* Ph have been investigated by the method of thermal analysis. Thermal diagrams have been obtained for mixtures of benzoin with each of the following substances:—Benzylaniline, benzylidene aniline, dibenzyl, azobenzene, benzil, hydrazobenzene, benzanilide, and also for mixtures of benzil with each of the following:—Dibenzyl, azobenzene, stilbene, hydrobenzoin, benzanilide. The diagram for benzylidene aniline—benzanilide has also been obtained. In all cases the thermal diagram has a V form, containing one eutectic point. In no case was there any evidence of compound formation, but solid solutions are formed to a limited extent in all cases. For benzoin eutectics both the temperature and concentration of the eutectic mixture is a function of the melting-point of the other constituent. This is seen from the table below:—

Benzoin Eutectics.

Substance.	Melting-point.	Eutectic temp.	Concentration. Per cent benzoin.
Benzylaniline ..	34·2° C.	32·4° C.	3
Benzylidene aniline	49·8	47·0	3
Dibenzyl	51·2	50·2	3·5
Azobenzene	66·2	63·8	6·0
Benzil	94·2	84·0	17·8
Hydrazobenzene ..	130·5	98·4	42
Benzanilide	160·8	116·6	64

The molecular volumes of the various substances have been determined. It is found that at the temperature of the melting-point the unsaturated substance has often a greater molecular volume than the saturated substance. No relation could be found between molecular volumes and eutectic points. Binary mixtures of benzylidene aniline, benzylanilme, stilbene, and dibenzyl with these substances are also discussed.

THE SATURATED ACIDS OF LINSEED OIL.*

By R. S. MORRELL, M.A., Ph.D.

A SUMMARY of the literature on linseed oil in Czapek's "Biochemie der Pflanzen," i., 121, and Lewkowitsch's "Oils, Fats, and Waxes" (fourth edition), ii., 50, shows that in addition to the unsaturated acids, linolinic, linolic, and oleic acids, the following saturated acids have been identified:—Palmitic and myristic acids in about equal proportions.

Haller (*Comptes Rendus*, cxlvi., 259, 1906), by fractional distillation of the methyl esters obtained from linseed oil, was able to separate appreciable quantities of palmitic and stearic acids and much smaller quantities of arachidic acid.

The occurrence of stearic acid in linseed oil seemed worthy of further investigation, not only for its practical importance, but also for its relationship to the unsaturated acids present. It is well known that when linseed oil is heated with lead oxide and allowed to cool a solid separates out, whose quantity is increased by addition of petroleum or turpentine. No record of a systematic investigation of this deposit has been published. The lead salts obtained from linseed oil from different sources were freed from unsaturated acids, and yielded a mixture of acid, melting-point 52—54° C., molecular weight 282—3, and iodine value 5—8. The acids consisted of stearic acid, with palmitic acid, and a trace of oleic acid. No myristic or arachidic acids were found. An investigation of the mixture by the methods recommended for the separation of saturated fatty acids has shown that it consists of 68 per cent stearic acid, and the remainder of palmitic acid, with 4·5 per cent oleic acid. The most satisfactory results were given by a combination of the methods devised by Hehner and Mitchell (*Analyst*, 1896, 321) and Kreis and Hafner (*Ber.*, 1913, xxxvi., 2766). The separation of the acids was very tedious, and a much more satisfactory method is desired. When more than two acids are present the quantitative separation is a matter of great difficulty.

* Read before the British Association (Section B), Birmingham Meeting, 1913).

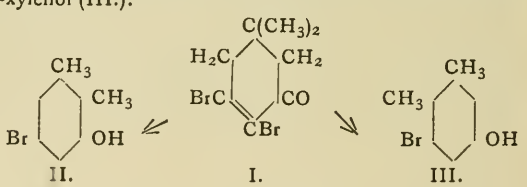
THE STUDY OF HYDROAROMATIC SUBSTANCES.*

1. *Bromoxylenols obtained from Dimethyldihydroresorcin* (*Proc. Chem. Soc.*, 1912, xxviii., 332).

DURING the past year work has been largely concerned with the transformation of certain hydroaromatic substances into bromoxylenols. These conversions were originally noticed during the action of phosphorus pentabromide on dimethyldihydroresorcin (*Journ. Chem. Soc.*, 1903, lxxxiii., 110), when the main initial products are not bromoxylenols, but are hydroaromatic in nature, the principal ones isolated being dibromo- and tribromo-dimethylcyclohexanones.

As the original reaction is very complicated, it was decided to study the transformations using the pure above-mentioned cyclic ketones, and as a result of the work so far concluded it has been established that—

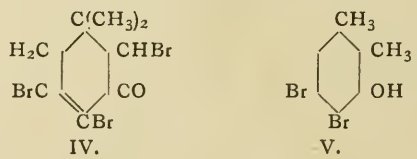
(*a*) The action of heat on dibromodimethylcyclohexenone (I.) gives rise to 5-bromo-*o*-3-xylenol (II.) and 6-bromo-*o*-4-xylenol (III.).



In the first of these rearrangements a methyl group has wandered, as previously noted, from carbon atom 1 to carbon atom 2; but in the second case from carbon atom 1 to carbon atom 6.

(*b*) The action of dilute alcoholic potassium hydroxide on dibromodimethylcyclohexenone gives rise to 5-bromo-*o*-3-xylenol and 4 : 5-dibromo-*o*-3-xylenol (V.).

(*c*) Tribromodimethylcyclohexenone (IV.) gives, under the influence of heat or alcoholic potassium hydroxide, mainly 4 : 5-dibromo-*o*-3-xylenol (V.) and another bromoxylenol, which has not so far been characterised.



The constitutions of 5-bromo-*o*-3-xylenol, 6-bromo-*o*-4-xylenol, and 4 : 5-dibromo-*o*-3-xylenol have been definitely established by synthetic methods (*Journ. Chem. Soc.*, 1913, ciii.).

* Report of the Committee, consisting of Prof. W. H. Perkin (Chairman), Prof. A. W. Crossley (Secretary), Dr. M. O Forster, Dr. H. R. Le Sueur, and Dr. A. McKenzie. Read before the British Association (Section B), Birmingham Meeting, 1913.

2. *Derivatives of Isopropyldihydroresorcin.*

The method for the preparation of isopropyldihydroresorcin (*Journ. Chem. Soc.*, 1902, lxxxi., 675) has been improved so as to yield 75 per cent of the theoretical amount of the dihydroresorcin.

1-Isopropylcyclohexan-3-ol and 1-isopropylcyclohexan-3-one have been prepared, and it is intended to use them as starting-points for the preparation of several meta-terpene derivatives.

THE STUDY OF PLANT ENZYMES PARTICULARLY WITH RELATION TO OXIDATION.*

The inquiry has been continued in various directions during the past year, as shown by the following list of communications to the Royal Society :—

(*a*) "Herbage Studies. II. *Lotus corniculatus* and *Trifolium repens*, Cyanophoric Plants." By H. E. Armstrong, E. F. Armstrong, and E. Horton.

(*b*) "Studies on Enzyme Action. XIX. Urease. II. Observations on Accelerative and Inhibitive Agents." By H. E. Armstrong, M. S. Benjamin, and E. Horton.

(*c*) "Studies on the Processes Operative in Solution (XXX) and on Enzyme Action (XX.). The Nature of Enzymes and of their Action as Hydrolytic Agents." By E. F. Armstrong and H. E. Armstrong.

(*d*) "Studies on Enzyme Action (XXI.). Lipase. III." By H. E. Armstrong and H. W. Gosney.

(*e*) "The *Rôle* of Oxydases in the Formation of the Anthocyan Pigment of Plants." By F. Keeble and E. F. Armstrong (in the "Journal of Genetics").

(*f*) "The Formation of the Anthocyan Pigments of Plants. IV. The Chromogens." By F. Keeble, E. F. Armstrong, and W. N. Jones.

(*g*) "The Formation of the Anthocyan Pigments of Plants. V. The Chromogens of White Flowers." By W. N. Jones.

(*h*) "The Formation of the Anthocyan Pigments of Plants. VI." By F. Keeble, E. F. Armstrong, and W. N. Jones.

Considerable progress has been made in elucidating the part played by oxidising catalysts in the production of plant pigments. By means of suitable agents—in particular benzidine and *a*-naphthol—oxydases and peroxydases can be localised in plants both in the flower petals and in the vegetative parts. Evidence has been accumulated in favour of the hypothesis that the soluble sap pigments of plants are formed by the oxidation of a colourless chromogen through the agency of an oxydase. The method has been applied with success to certain problems in genetics.

The sap pigment may be reduced to the colourless chromogen by the agency of a reducing substance. Such a change takes place when the coloured cell is stimulated by a hormone (a substance which penetrates the cell membrane) under conditions in which the amount of water present is a minimum. When the conditions are reversed and there is an excess of water in the system, the chromogen is reoxidised. Both the reducing substance and the reduced pigment are soluble in aqueous alcohol of a suitable strength (90 per cent). After extraction of a coloured petal by alcohol of this strength, both the solution and the extracted petal are colourless; but they can be caused to recover their original colour—the solution on evaporation of the alcohol and dissolution of the residue in water, the petal on warming in water. There is evidence that the flower contains an excess of chromogen beyond that normally converted into pigment. The reducing substance is not destroyed by boiling; it cannot therefore be classed as an enzyme. The experiments afford proof of the existence of an oxidising-reducing mechanism in the cell sap which controls the formation of flower colour and is itself regulated by the condition of concentration of the cell sap. Dilution favours oxidation, concentration alters the balance in the opposite direction.

Very little progress has yet been made in determining the chemical nature of the sap pigments. The researches of A. G. Perkin have made it almost certain that the soluble yellow pigments belong to the class of hydroxyflavones of which quercetin is the best known representative. On genetical grounds there is strong evidence in favour of regarding these yellow pigments as antecedents of the red, magenta, and blue sap pigments. By hydrolysis and subsequent reduction and oxidation or by hydrolysis and oxidation, red pigments have been obtained from a number of yellow flowers, such, for example, as the wallflower, daffodil, and primrose; it is possible that the coloured varieties of these species may arise in a similar manner.

The most fruitful discovery during the year has been the proof afforded by Chodat that the action of tyrosinase on an amino-acid, *e.g.*, glycine, gives rise to the production of formaldehyde, ammonia, and carbon dioxide. Elements are thus available for the production of all manner of complex compounds and the method has a wide application. Starting, for example, from a mixture of the glucoside arbutin with glycine, it is possible, by the action of emulsin and an oxydase at the ordinary temperature, to obtain first a red compound, then a brownish black substance, as well as a volatile compound possessing the characteristic odour of ripe plums. In short, both the colour and odour of the ripe fruit are obtained by a biological synthesis from the glucoside and an amino acid. This synthesis appears of general application, and is being further studied. Presumably the colours produced in this manner are those characteristic of the fruit and leaves of the plants rather than of the flower petals. The interaction appears to involve the oxidation of the phenolic constituent of the glucoside either to an *ortho-* or to a *para*-quinone, the condensation to quinhydrone and the interaction of this compound with ammonia and formaldehyde. *Meta*-phenols do not undergo the same transformation.

* Second Report of the Committee, consisting of Mr. A. D. Hall, (Chairman), Dr. E. F. Armstrong (Secretary), Prof. H. E. Armstrong, Prof. F. Keeble, and Dr. E. J. Russell. Read before the British Association (Section B), Birmingham Meeting, 1913.

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

The Transformation of Acylchloroaminobenzenes and the Chlorination of Anilides. The Reactions of Chloroamines in Aqueous Solution. (With W. H. Gray, B.Sc.).

In a previous report (*Reports*, 1910) we have given a summary of the results of a large number of experiments on the transformations of chloroamines into the isomeric chloroanilides, $Ar.NCl.Ac \rightarrow ClAr.NH.Ac$; it was shown that this change could not be regarded as an intramolecular rearrangement, but consisted primarily of a reversible reaction of hydrogen chloride with the chloroamine; thus,—

$$Ar.NCl.Ac + HCl \rightarrow Ar.NH.Ac + Cl_2 \rightarrow ClAr.NH.Ac + HCl,$$

followed by a direct irreversible interaction of chlorine and the anilide.

In these experiments the medium was aqueous acetic acid containing not less than 50 per cent of acetic acid.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, and Dr. J. T. Hewitt. Read before the British Association (Section B), Birmingham Meeting, 1914.

We have now examined the behaviour of acetylchloroaminobenzene in pure aqueous solution, and have discovered an interesting modification of the ordinary reaction.

The production of hydrogen chloride during the transformation of a chloroamine, in the presence of hydrogen chloride, was first indicated by Blanksma (*Recueil des Trav. Chim.*, 1903, xxii., 290), who found that the amount of this acid at the end of the reaction was slightly greater than that originally introduced. Moreover, it was demonstrated by Chattaway and Orton (*Proc. Chem. Soc.*, 1902, xviii., 200) that any change of the chloroamine which occurred in the presence of other acids—for example, sulphuric—was invariably acccompanied by the appearance of hydrogen chloride. The first quantitative experiments were made by Orton and Jones (compare *Reports*, 1910). These were carried out in an acetic acid medium containing from 0—35 per cent of water, both in the presence and absence of various acids. Table I. shows some of the results.

TABLE I.

Medium. Per cent.	Acid.	Time of reaction Days.	Chloroamine disappeared. Per cent.	Chloroamine reduced. Per cent.
65 HA	None	22	50·8	6·04
„	H_2SO_4	13	49·16	11·2
„	HNO_3	7	54·96	3·72
„	$HClO_4$	9	48·0	18·67

The following experiment serves as a comparison when a chloroamine, which cannot yield an isomeride, is used :—

65 per cent HA H_2SO_4 16 days 8·25 per cent 8·1 per cent

In the following experiments hydrogen chloride (1 molar proportion) is initially present :—

	Per cent.
Glacial puriss. Reaction complete	3·24
Glacial ordinary. Reaction complete ..	6·0
93·4 per cent puriss Reaction complete ..	1·96
75 per cent puriss. Reaction complete ..	1·84

There can be little doubt as to the manner of this reduction. In all aqueous media some hydrolysis of the chloroamine occurs : —

$$Ar.NCl.NAc + H_2O \rightleftarrows HClO + Ar.NH.Ac.$$

The reduction of hypochlorous acid is rapid in aqueous acetic acid even when carefully shielded from light. From an aqueous solution of chloroamine it is possible to distil off hypochlorous acid under reduced pressure. Thus at 25° and under 13·9 mm. the first 50 cc. of distillate from 250 cc. of a 0·1 per cent solution of a chloroamine bad a titre of 2·57 cc. of N/20 thio. No chlorine was found in the distillate, and there was no loss of chloroamine from the mother-liquor other than by hydrolysis. The distillation of an equivalent solution of hypochlorous acid showed that the hydrolysis of the chloroamine is not extensive ; for the first 50 cc. gave a titre of 30 cc. N/20 thio.

Reduction of the Chloroamine in Aqueous Solution.—The behaviour of acetylchloroaminobenzene in pure water would be expected to show a marked difference from that in concentrated acetic acid media on several grounds. If it be granted that the mechanism of the isomeric transformation consists in a reaction between chloroamine and hydrogen chloride, yielding anilide and chlorine, which then react to form the C-chloro derivative, any extensive hydrolysis of the chlorine should lead to abnormalities and retard the production of chloroanilides. Jakowkin (*Zeit. Phys. Chem.*, 1899), showed that the reversible hydrolysis of chlorine, which is governed by the equation $K[Cl_2] = [HClO][HCl]^2$, is very extensive in dilute aqueous solution. Thus, for example, over 90 per cent of the chlorine at a concentration of 0·05 per cent and less is present as hypochlorous and hydrochloric acids. From the form of the equation it will be seen that the proportion of free chlorine in the system would rapidly increase as the concentration of hydrogen chloride was raised ; according to Jakowkin in solutions of hydrogen chloride above 0·1 N very little of the chlorine is present as hypochlorous acid. Above these limits of concentration of hydrogen chloride, therefore, the ordinary conversion of chloroamine would predominate.

Our experimental study is generally in harmony with these anticipations. With a high concentration of hydrogen chloride, the main reaction is a transformation of the chloroamine into monochloroacetanilides, but with low concentrations the reactions are greatly modified. In fact, the behaviour with hydrogen chloride then closely resembles that with other acids.

Aqueous solutions of acetylchloroaminobenzene change very slowly if due regard is had to the purity of the water and the protection of the solution from contamination with reducing materials. At 25° a 0·1 per cent aqueous solution of this chloroamine drops only a few per cent in titre in the course of several weeks ; at 60°, however, 50 per cent has disappeared in 38·5 hours. The addition of small quantities of an acid (1 to 2 molecular proportions, which give a concentration of 0·0058 to 0·0116) increases the rate of change, which is, however, still very slow ; about 50 per cent of the chloroamine disappears in one month at 25°, but in less than a day at 60°. There is no great difference between different acids, including hydrochloric, in their effect. Careful examination of the reactions, which lead to a fall in titre both in aqueous and highly dilute acids, discloses the fact that the principal change is a simple reduction of the chloroamine to anilide and hydrogen chloride ; at the same time a small and very variable amount of chlorate appears. The production of chloroanilides is quite subsidiary. The most obvious interpretation of the facts is that the chloroamine is hydrolysed :—

$$Ar.NCl.Ac + H_2O \rightleftarrows HClO + Ar.NH.Ac,$$

and the hypochlorous acid then reduced. It is not so easy to see how the latter change is brought about. Both an aqueous solution of hypochlorous acid and also solutions containing a strong acid are quite stable. Moreover, the pure anilide does not reduce hypochlorous acid ; the sole interaction is the equilibrium represented above. It seems most probable that the reduction is effected by aniline arising from the hydrolysis of the anilide—a change which has been shown to occur, but slowly, under the circumstances. The hydrolysis of the anilide in pure water is yet slower than in acids, and hence the permanence of solutions of chloroamine in this medium at ordinary temperatures. The development of the characteristic colour reactions of aniline with hypochlorous acid in the course of the change is in harmony with this suggestion. Further aniline is particularly effective is a reducing agent for hypochlorous acid, since one molecular proportion reduces several of the acid.

At higher concentrations of the acids (0·023 N) the specific effect of hydrogen chloride appears ; but with the other acids the speed of hydrolysis and reduction is merely increased. But even with very great excess of hydrogen chloride, when the disappearance of the chloroamine is relatively rapid, the hydrolysis and reduction can still be detected as a subsidiary reaction. The formation of hydrogen chloride by reduction in the experiments with other acids is the obvious cause, as previously indicated, of the production of the small quantities of chloroanilide.

Method of Experiment.- Aqueous solutions of acetylchloroaminobenzene containing about 1 grm. per litre were used, the reactions being carried out at 25° and 60°. After more than 50 per cent of the chloroamine has disappeared, the hydrogen chloride is estimated. The remaining chloroamine (and the very small amount of hypochlorous acid) is reduced by arsenite, and the chloridion weighed as silver chloride. In order to estimate any chlorate which has been formed from the hypochlorous acid the reduction in another portion is carried out by sulphite. The chloroanilide is assumed to be given by difference, but it is quite possible that some chlorine disappeared in the oxidation of

the aniline or in chlorinating free aniline. Some of the results are shown in Table II.

TABLE II.

Acid.	Temperature.	Percentage of chloroamine converted into— (a) Cl′.	(b) Cl′+ClO$_3$′.	(c) Chloroanilide.
HCl (2 mols.) ..	25°	54·24	8·12	37·64
H_2SO_4 (1 mol.) ..	25°	68·77	12·74	18·52
H_2SO_4 (4 mols.) ..	25°	65·39	15·46	19·14
HNO_3 (1 mol.) ..	25°	76·56	5·59	17·85
$(COOH)_2$ (1 mol.) .	25°	74·36	—	25·64
HCl (10 mols.) ..	25°	12·2	—	87·78
HCl (20 mols.) ..	25°	7·73	—	92·28
HCl (4 mols.) ..	60°	25·42	3·93	70·65
HCl (10 mols.) ..	60°	11·47	—	88·54
HCl (2 mols.) ..	58·5°	43·76	9·36	46·98
Water	60°	63·59	—	36·42
H_2SO_4 (1 mol.) ..	60°	60·85	12·19	26·96
H_2SO_4 (10 mols.) .	60°	73·86	0·91	25·23

The times which the reaction occupies in various cases are very different. The chlorination of the anilide is in an aqueous medium an extremely rapid reaction (Orton and Jones, *loc. cit.*), and hence in circumstances when chlorine and anilide are present at relatively high concentrations, the chloroamine rapidly disappears, and a large proportion of chloroanilide is formed. This condition is realised when the concentration of the hydrogen chloride is sufficiently raised, for, as was shown in the foregoing, the hypochlorous acid is then replaced by chlorine:— $H' + Cl' + HClO \longrightarrow Cl_2 + H_2O$, and further hydrolysis of the chloroamine follows from disturbance of the equilibrium: $Ar.NCl.Ac + H_2O \longrightarrow Ar.NH.Ac + HClO$.

The time of the half-change in a number of the experiments is shown in Table III.

TABLE III.

Expt.	Acid.	Temp.	Half-period.	Percentage of chloroanilide.
i.	HCl (2 mols.) ..	25°	16·75 days	37·64
ii.	HCl (2 mols.) ..	60°	8·2 hours	43·6
iii.	HCl (4 mols.) ..	60°	2·8 hours	70·65
iv.	HCl (10 mols.) ..	60°	40·5 mins.	88·54
v.	H_2SO_4 (1 mol.) ..	25°	31·5 days	18·52
vi.	H_2SO_4 (4 mols.) .	55°	11·3 days	19·14
vii.	H_2SO_4 (1 mol.) ..	60°	18·7 hours	26·96
viii.	H_2SO_4 (10 mols.)	60°	4·9 hours	25·23

(i.) A comparison of the experiments in which hydrogen chloride was used with that in which sulphuric acid was used at equivalent concentration (i. with v. and ii. with vii.), whether at 25° or 60°, shows that with double the production of chloroanilide, the speed of the disappearance of chloroamine is also approximately doubled.

(ii.) With increase in the concentration of the hydrogen chloride the production of chloroanilide rapidly increases. Raising the proportion of hydrogen chloride from 10 to 20 mols. roughly quadruples the speed, but only slightly raises the proportion of chloroanilide (from 88 to 92 per cent).

(iii.) Increase in the concentration of the sulphuric acid is accompanied by an increase in the rate of disappearance of the chloroamine. But in marked contrast to the effect of hydrogen chloride, the reaction is still identical; the production of chloroanilide and the reduction remain in the same proportion.

These results illuminate some recent observations of Rivett (*Zeit. Phys. Chem.*, 1913, lxxxii., 201) on the "transformation" of acetylchloroaminobenzene in aqueous solution. In one series of experiments he used hydrogen chloride, but never below a concentration of 0·1351. Although the values for—

$$k_1/[HCl]^2 (= 0{\cdot}0413 — 0{\cdot}0419)$$

between the limits of 0·2702—0·4797 for [HCl], are very close, he seeks for an explanation of the slightly divergent values outside these limits of concentration only in the degree of ionisation of the hydrogen chloride, and in the secondary influences of the ions on one another or on the unionised molecules on the ions. Our demonstration of the existence of a subsidiary side reaction would indicate another cause for the divergence from strict constancy of the expression $k_1/[HCl]^2$. We have previously attempted (*Reports*, 1910) to show how this relation, $k_1/[HCl]^2$ = const., is accounted for on our view of the transformation.

The speed of the formation of chloroanilides is given by the equation:—

$$d[\text{chloroanilide}]/dt = (k_{II}[Cl_2]\ [\text{anilide}] = = k_{II}K[\text{chloroamine}][HCl]^2.$$

Since

$$K[\text{chloroamine}][HCl]^2 = [Cl_2][\text{anilide}],$$

from the equilibrium:—

$$Ar.NCl.Ac + H' + Cl' \rightleftarrows Cl_2 + Ar.NH.Ac;$$

hence as chloroamine is the only variable—

$$d[\text{Chloroanilide}]/dt = (k_{II}.K[HCl]^2)[\text{chloroamine}] = = k_1[\text{chloroamine}].$$

Apart from the completeness of the ionisation of the hydrogen chloride, and apart from the slight increase in the concentration of the hydrogen chloride during the reaction, the quantity of chloroamine in the equation is supposed to be sensibly identical with that used in the preparation of the system, the reaction with hydrogen chloride being disregarded. These approximations would undeniably cause variation in the expression, $k_1/[HCl]^2$.

The final form of the equation is not changed if the hydrolysis of the chloroamine is taken, as seems necessary in an aqueous medium, as the first step.

$$Ar.NCl.Ac + H_2O \longrightarrow Ar.NH.Ac + HClO \text{ and}$$

$$H' + ClHClO + ' \rightleftarrows Cl_2 + H_2O.$$

For

$$K_a' \text{Chloroamine}][H_2O] = [\text{anilide}][HClO],$$
$$K_b[Cl_2][H_2O] = [HClO][HCl]^2,$$
$$K_a[\text{Chloroamine}]/K_b[Cl_2] = [\text{anilide}]/[HCl]^2,$$

or

$$K[\text{Chloroamine}][HCl]^2 = [Cl_2][\text{anilide}].$$

In Rivett's experiments with a pure aqueous medium, and also with other acids, he fails to recognise that the transformation of the chloroamine to the chloroanilides is merely a side-reaction, and that hydrolysis and reduction are the primary changes. His measurement of the rate of disappearance of chloroamine in these solutions led him to the conclusion that hydrogen chloride was produced, but he does not determine the amount of hydrogen chloride, and thus misses this fact. Without attempting to examine his views as to the series of changes (reversible) by which he supposes hydrogen chloride to be produced, it may be stated that he does not suggest the reduction of chloroamine or hypochlorous acid. Moreover, it may be pointed out that the pink or purple colour referred to above, which appears during the decomposition of the chloroamine, is without doubt identical with the ordinary colour reaction of bleaching powder and aniline, and not as is suggested due to a compound, Ar.N*x*.Ac, produced together with hydrogen chloride in a reversible reaction with the acid: $Ar.NCl.Ac + Hx \rightleftharpoons Ar.Nx.Ac + HCl$.

Summary.

1. The decomposition of acetylchloroaminobenzene in pure aqueous solution, or in the presence of all acids including hydrochloric, at a very low concentration is mainly hydrolysis and reduction of the hypochlorous acid:—

$$Ar.NCl.Ac + H_2O \longrightarrow Ar.NH.Ac + HClO$$
$$Ar.NH.Ac + H_2O \longrightarrow Ar.NH_2 + CH_3.CO_2H$$
$$x(HClO) + Ar.NH_2 \longrightarrow (Ar.NH_2 + xO) + xHCl.$$

The transformation of the chloroamine into chloroanilides, which follows from the formation of hydrogen chloride, is quite subsidiary.

2. With higher concentrations of hydrogen chloride, more chlorine appears in the system from the reaction $\cdot H' + Cl' + HClO \rightarrow Cl_2 + H_2O$. According to Jakowkin's measurements, chlorine is nearly completely hydrolysed in water at concentrations below 0·05 in the absence of excess of hydrogen chloride, whilst on the other hand in solutions of hydrogen chloride above 0·1 N, hydrolysis of the chlorine is nearly absent. Hence, now that chlorine and anilide are both at relatively high concentrations, the transformation of chloroamine to chloroanilide is the main reaction.

3. With acids other than hydrogen chloride, increase in the concentration cannot cause a similar change in the reaction.

4. The results of the study of the decomposition of chloroamine in aqueous solution are in complete harmony with the earlier view as to the part played by hydrogen chloride in the conversion of chloroamines to the isomeric chloroanilides.

The Committee asks to be reappointed with a grant of £20.

The Report is a summary of the work which has been carried out. A detailed account of the experimental work will be published later in one of the Chemical journals.

FLAVOUR OF BUTTER INJURED BY METALS

Economic conditions make it necessary at present to hold butter in storage from the summer season, when it is plentiful, to the winter season, when it is scarce. If the butter is properly made this can be done without materially injuring its quality. It often occurs, however, that butter which has been held in storage for some months develops disagreeable flavours that greatly lessen its value. These bad flavours that will often pass unnoticed when the butter is fresh, may become so serious a defect after three or four months in storage as to render the butter almost unsaleable. The chemical changes which cause these bad flavours are often too small to be detected by the ordinary analytical methods of the laboratory, but the senses of smell and taste are far more delicate, and soon as bad flavours are detected by them the value of the product is lessened.

Some metals either cause or greatly accelerate certain bad flavours in butter, although most of the experiments along this line have not included storage butters. Recently the scientific staff of the Dairy Division of the Bureau of Animal Industry in the United States Department of Agriculture has reported that the presence of very small amounts of iron in cream causes certain undesirable flavours to increase in intensity during storage. These flavours are often designated by butter experts as "metallic," "oily," or "fishy." The injurious effect of iron was found by adding iron in known quantities, varying from 1 to 500 parts, to a million parts of cream. The butter made from such cream was compared with that made from cream where all precautions were taken to avoid any undue contact with iron during the whole process of butter making. The butter was stored at 6° to 10° Fahrenheit, and the quality of the butter was scored by experts at different times. In every instance when the butter was scored a few days after making, the samples to which iron had been added scored lower than the butter made from cream which contained no iron. This held true in most cases on the second and third scoring, which occurred at intervals varying from 20 to 187 days. The most noticeable feature was the rapid development of bad flavour in the butter containing the iron. When both the control and the experimental butter became fishy it was noticed that the control butter was the last to become so. There was a marked oily flavour present in most samples that subsequently became fishy. Only a small proportion of the iron added to the cream was found in the butter, the remainder having been taken up by the buttermilk and wash water.

Butter was also made from cream which had stood in rusty cans, and in every case this butter had a peculiar taste and was easily picked out from all other samples. The buttermilk also had a decided metallic taste.

The influence of copper on the flavour of butter was studied in a similar manner, and it was found that copper, even in small quantities, seemed to cause more marked changes of flavour in butter than did the iron, with a decided tendency toward a fishy flavour in storage. Two experiments showed very plainly the harmful effect of using poorly tinned pasteurisers, even though the cream came in contact with the copper surface for only a few seconds, for, aside from this, all other conditions were exactly alike during the complete process of butter manufacture.

This work shows that if cream is kept in rusty cans or comes in contact with iron or copper at any time during the process of butter making it may take up iron or copper from rusty cans, exposed bolt heads, or other metal parts of pasteurisers or churns, in sufficient quantities to affect the flavour of storage butter. Though there is nothing to show that the nature of the flavour is appreciably changed, it does demonstrate very clearly that the rate of development of the undesirable flavour is greatly accelerated during storage by very small quantities of either iron or copper.—*Chemical Engineer*, xviii., No. 1.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Supremacy of Iron.

France, who less than thirty years ago occupied an unfavourable rank amongst the producers of iron, has risen during the last few years to one of the first rank. It is especially the increase in the production of the Eastern mining region that raised France from the fifth or sixth place to the third. The mineral production in France in 1912 certainly exceeded a total of 18 millions of tons. The United States holds the world's record with a grand total of 60 million tons. Germany is second with 25 million tons. France comes next, then England, with 16 millions, and Spain with 10 million tons of iron ore. The quantity of iron extracted from the basin of Briey in the Meurthe-et-Moselle district has doubled in less than four years. From 6,000,000 tons in 1909 the production in this region has gone up to 12,000,000 tons in 1912. The department of Meurthe-et-Moselle alone, with its basins of Nancy, Longwy, and Briey, produced in 1912 about 17,000,000 tons of iron ore. All the other mining districts of France scattered from the Pyrenees and Anjou to Normandy produce about 1,000,000 tons. But the production of the basin of Caen will soon, doubtless, be considerably increased. An eminent geologist, M. Bailly, had estimated that the basin of Briey would not reach its normal maximum production before 1970, with a total of 35 million tons. It is probable, however, that this maximum will be reached much sooner. The consumption of sheet iron, iron, and steel is increasing enormously throughout the world. In the struggle that the nations are engaged in for the supremacy of iron, France is well armed. She will easily be able, as soon as she wishes, to take the second rank among the nations of the world.

General Topographical Levelling of France.

The Minister of Public Works is at present undertaking the completion of the third and last general levelling of France. When this operation is finished the total length of levelling will comprise no less than 100,000 kilometres. This gigantic work was undertaken in 1855 by Bourdaloue,

Chief Engineer of the Road-surveying Department, but it is especially since 1884, under the active direction of another engineer, M. Lallemand, that the enterprise has been pushed on with great activity. The general levelling of France included four systems. Their network of meshes, the size of which grows gradually smaller, cover the whole extent of the territory. The first and most important system, called also the basis system, has a development of 1200 kilometres, with meshes of which the circumference varies from 400 to 600 kilometres. Finished in 1892 it was traced with such precision that the initial altitude has been met with again, with only about 6½ centimetres difference after the whole tour of France had been effected; that is to say, after a distance of 3908 kilometres. It is now fifteen years since the system of the second order has been completed, the meshes vary from 300 to 400 kilometres in width. The system of the third rank is almost terminated; of 47,000 kilometres in length it has meshes of from 60 to 100 kilometres round. Lastly, the fourth and last system has meshes of only 10 to 20 kilometres round. It is expected that it will be completely traced in four or five years time, and thus the general levelling of France will be completed with the utmost precision. This is an occasion to call to mind here that the zero of altitudes that served as a basis for this gigantic operation is to be found at Marseilles. It is placed on the tidal scale, which is fixed on an angle of St. John's Quay, at the foot of the port near the trans-shipping bridge; but what is generally totally unknown is the reason of such a choice. The engineers of the period thought that in the Atlantic, as in the Channel, the average levels, taken in several seaports, did not coincide; that, moreover, the tides might be prejudicial to the determination of this level; that this disadvantage did not exist in the Mediterranean, and that, on the contrary, only very insignificant differences of level had been observed at several points of the Gulf of Lyons. It is at the tidal Observatory of the Corniche that is kept the rivet of iridised platinum that constitutes the fundamental guiding mark for the levelling of the country of France. And the mark is established, naturally, according to the zero of St. John's Quay. That is how it is that, since January 13, 1860, Marseilles has the honour of possessing the zero of altitudes. However, it is now recognised that this measure is somewhat arbitrary. It has been remarked that, following on certain atmospheric conditions, the level of the sea is subject to fluctuations, and that it is materially impossible to trace on any point whatever of the coast a sea level that would be mathematically invariable—that, in a word, would be the average type level.

A Wood that Never Rots.

Engineers have often to deplore the rotting of railway sleepers, of piles, and of wood used to support galleries, in the building of ships, &c. Engineers, chemists, physicists, biologists, doctors, who, for the construction of diverse apparatus, may require a wood possessing a maximum resistance to the causes of destruction, particularly humidity, are interested in this important question of the unputrescibility of wood. The ideal would be to find a wood of a character susceptible of resisting putrefaction naturally. Now it appears from recent researches that the wood of the mangrove tree may be considered as absolutely unputrescible. Numerous samples of mangrove wood (*Rhizophora racemosa*) sent from French Guinea were, in 1909, placed at Collonges (Côte d'Or) in a soaking pit in the depot of sleepers of the Paris-Lyons-Mediterranean Railway Company. The samples were surrounded with all the elements susceptible of producing the decomposition and rotting of the wood in a minimum of time. In spite of these precautions the samples have up till now remained in an excellent state, and show no signs of the least alteration. Why is putrefaction unable to attack the wood of the mangrove? From whence do the particular and excellent qualities of this too little known wood proceed? It is first of all to be remarked that the grain of the mangrove wood is very close; for this reason it opposes a barrier to the invasion of water, by a quasi-mechanical action. To get an idea of the importance of this fact, it suffices to examine comparatively the densities of the woods of the mangrove, oak, and fir. The first is about 110, the second 70, and the third 40. Moreover, mangrove wood has an amount of tannin quite sufficient to prevent the invasion of insects and to prevent the multiplication of germs, damp, mould, and all various micro-organisms which constitute the flora of the woods of different climates. The wood of the mangrove marvellously resists flexion; its resistance is double that of oak, quadruple that of fir; nevertheless, it is not at all brittle. To crushing either at the end or across the fibres it offers a resistance double that of oak and three times that of fir. It resists admirably the efforts of wringing or twisting, far better than the two other woods mentioned, to which it is far superior in suppleness. With these qualities just enumerated it is easily worked; it is as easily sawn as the oak. From the few preceding remarks we may conclude that the wood of the mangrove merits employment on a large scale and for purposes both numerous and varied. Henceforth its use appears to be indicated for the construction of the posts of electric lines on account of its unputrescibility, its resistance, and its suppleness. Its resistance to putrefaction and to crushing render it precious for the construction of sleepers of narrow railways. Its use would be advantageous compared with other woods for the special wood-work of mines, where it would offer all the qualities required by hygiene. And, besides, everyone will find good use for a wood that never rots.

The Ignition of Wood.

The substance the most employed to prevent the ignition of wood is silicate of potassium in solution; the wood is soaked in it, which protects it for a long time from all danger of inflammability. But several successive layers are necessary in order to arrive at a really efficacious immunisation. The following is a good recipe:—35 per cent of silicate of potassium, 35 per cent of sulphate of baryta, from 1 to 2 per cent of zinc white, and lastly 28 per cent of water; but it is not the only recipe. The greater number, however, are trade secrets. M. Wolff considers of great importance the impregnation of the wood with alum in order to render it incombustible; this process, however, does not appear to be in use. It was indeed noticed that during the fire of the alum manufactory of Muskan the fire spared all the beams that had long been exposed to the vapours of alum.

NOTICES OF BOOKS.

An Introduction to the Chemistry of Plant Products. By Paul Haas, D.Sc., Ph.D., and T. G. Hill, A.R.C.S., F.L.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The student of vegetable physiology is but ill-equipped for his work unless he has a knowledge of the elements of organic chemistry, and, moreover, he needs to have a special acquaintance with certain branches which are not usually included in an elementary course. This book is designed to give him this knowledge of the facts and phenomena which are of particular importance in botany, and it is intended to be used after a preliminary course in theoretical and practical organic chemistry. Beginning with the fats and oils and passing on to carbohydrates, glucosides, tannins, &c., the authors describe the preparation, reactions, and methods of estimation of all the commoner compounds. The subject is treated both theoretically and practically, and copious references are given to the literature of biochemistry.

The Synthetic Dyestuffs and the Intermediate Products from which they are Derived. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen), and JOCELYN FIELD THORPE, D.Sc. (Manchester), Ph.D. (Heidelberg), F.R.S., F.I.C. Second Edition, London: Charles Griffin and Co., Ltd. 1913.

IN the second edition of this excellent laboratory text-book on the synthetic dyestuffs the general plan and arrangement of the first edition is preserved, the first part giving a theoretical description of the intermediate products and dyestuffs, the second part dealing with their preparation, while in the third part their analysis and identification are discussed, and methods of detecting dyestuffs on the fibre are explained. In this section Green's tables are now reproduced in full, and repiace those given in the first edition. The chapter on Oxyketone Dyestuffs is now headed "Anthracene Dyestuffs," and includes indanthrene and similar products, and the new indigoid colouring matters are now treated fully. Many new azo compounds are also described for the first time, and the names of some typical members of the various sub-sections have had to be changed in the new edition.

OBITUARY.

PROFESSOR HUGH MARSHALL.

WE regret to have to announce the death of Prof. Hugh Marshall, F.R.S., D.Sc., at the early age of 45.

Prof. Marshall, who was a native of Edinburgh, received his early education in that city, and proceeded from the University there to Munich and afterwards to Ghent. He was appointed Lecturer in Mineralogy and Crystallography at the University of Edinburgh in 1894, and in 1902 he became Lecturer in Chemistry at the same University. In 1908 he was appointed Professor of Chemistry at University College, Dundee. Dr. Marshall devoted himself chiefly to the study of crystallography, and published some important papers on this and allied subjects. He also investigated the metallic salts of some organic acids, and was the joint author of books entitled "An Introduction to Chemical Crystallography" and "Salts and their Reactions." He was elected a Fellow of the Royal Society in 1904.

SIR WALTER HARTLEY.

BY the death of Sir Walter Noel Hartley, F.R.S., D.Sc., which occurred on September 11th at Braemar, the Royal College of Science, Dublin, has suffered an irreparable loss, which will be shared by the whole scientific world. Sir Walter Hartley, who was knighted in 1911, was Professor of Chemistry and Dean of Faculty of the Royal College of Science, and was formerly Vice-President of the Institute of Chemistry. In 1903-4 he was President of the Chemistry Section of the British Association, and was a Fellow of King's College, London.

His most famous scientific investigations were in the region of spectroscopy, where he contributed many valuable results of great practical and theoretical importance. He first suggested the employment of an alloy of cadmium, tin, and lead for the purpose of obtaining a spark spectrum which could be used as a standard of comparison, and this alloy has been found to give highly satisfactory results. He also devised a new form of apparatus for obtaining the spark spectra of metallic salts, and made an exhaustive study of the spark spectra of metals and their salts, from which very important conclusions can be deduced. He was a pioneer in the determination of wave-lengths in the ultra-violet region and also in the investigation of the banded spectra of metals obtained in the oxyhydrogen flame. He carried out a long series of experiments on ultra-violet absorption spectra, extending his observations to the case of organic compounds, and publishing his first paper on the subject in the *Philosophical Transactions* in 1879. He conceived the idea of studying the absorption limits of substances at a great many different concentrations, and by plotting the absorption curves deduced from his results he was able to draw very valuable inferences regarding the relation between chemical constitution and absorption spectra. By the use of his method it is possible to determine the molecular constitution of many substances for which chemical methods fail. He investigated the question of the appearance of series of lines in spectra, and studied the relationship between the doublets and triplets in some metallic spectra. He was much interested in the application of photography to the solution of chemical problems, and also published papers on colour changes in some chemical compounds, and on the theory of colour. He was a frequent contributor to the *Philosophical Transactions*, the *Proceedings of the Royal Society*, the *Transactions of the Chemical Society*, and the CHEMICAL NEWS, and wrote a paper which appeared in Kayser's "Handbuch der Spectroscopie" in 1905. He was awarded the Longstaff Medal of the Chemical Society for research in Spectrochemistry in 1906, and the Grand Prix for Spectrographic Research at the Franco-British Exhibition in 1908. He was the author of "Air and its Relations to Life," 1876; "Water, Air, and Disinfectants, 1877"; and "Quantitative Analysis for Students," 1877.

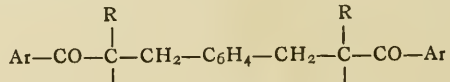
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 1, July 7, 1913.

Acetyl-acetonates of Cerium.—André Job and Paul Goissedet.—Ceric acetyl-acetonate can be prepared by suspending ceric hydrate in water, adding excess of acetylacetone, and shaking. A brown colouration appears, and after several days very dark red crystalline needles separate. They are the normal ceric acetyl-acetonate, CeR_4, with 11 molecules of water. The anhydrous compound may be obtained by evaporating a solution in carbon tetrachloride. It is a black metallic crystalline substance which yields a brown powder when crushed.

Diketones obtained by the Action of Xylylene Dibromides on Isopropylphenyl Ketone and their Decomposition by Sodamide.—M. Dumesnil.—The author has proved that when sodamide acts on diketones or the formula—



diamides are obtained having NH_2 groups in the place of the Ar groups. The diamides can be converted into the corresponding acids by heating with 50 per cent sulphuric acid for six hours in a sealed tube to 150°.

Hydrogenation of α-Ethylenic Secondary Alcohols in presence by Nickel.—Roger Douris.—At a temperature of about 200° propenylisoamylcarbinol, vinylisobutylcarbinol, propenylcyclohexylcarbinol can be hydrogenated over nickel, yielding the corresponding ketones. The saturated hydrocarbons corresponding to the alcohols employed are formed at the same time.

No. 2, July 15, 1913.

Fluorine in the Animal Organism.—Armand Gautier and P. Clausmann.—Fluorine exists in all animal tissues and organs, but in very different amounts, varying from 180 mgrms. to 0·15 mgrm. per 100 grms. of dry matter. It always accompanies phosphorus, to which it appears to be bound. The quantity of it may differ very much in different regions of the same tissue, and it varies with the age of the individual, generally increasing up to maturity, and then decreasing. Muscular tissue is very poor in fluorine, while the blood is relatively rich.

Action of Ultra-violet Rays on Hydrogen Peroxide.—Victor Henri and René Wurmser.—The rate of decomposition of H_2O_2 in monochromatic light is proportional to the concentration, the reaction being monomolecular. For each wave-length it is proportional to the incident energy, and it is also proportional to the energy absorbed, the factor of proportionality being the same for wave-lengths between 2800 and 2060. Einstein's law of photochemical equivalence does not hold good for the decomposition of H_2O_2. The energy absorbed in the decomposition of a grm.-molecule of H_2O_2 is practically equal to the energy liberated by the decomposition of H_2O_2 in the dark.

Additive Reactions of Carbon Monoxide with other Gases under the Influence of the Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—The tendency of CO to give addition products under the influence of light is specially marked with the first members of the different series. Thus it combines with Cl but not with Br or I, with O but not with S, with H_2O but not with H_2S, and with NH_3 and not with PH_3 or AsH_3. These first members are those which have the most important rôle in nature, and the union of CO under the action of light with H, O, H_2O, and NH_3 is of great biochemical importance.

Formation of Methane by Catalysis from Carbon Monoxide and Water Vapour.—Léo Vignon.—The following substances act as catalysts, transforming CO into CH_4 in the presence of water vapour:—Al_2O_3, MgO, SiO_2, Fe, Ni, Cu. The mechanism of the transformation differs in different cases. With Fe, Al_2O_3, SiO_2, carbides are first formed, and then decomposed by the water vapour:—

$$12CO + 2Al_2O_3 = C_3Al_4 + 9CO_2,$$

$$C_3Al_4 + 6H_2O = 3CH_4 + 2Al_2O_3.$$

Some hydrogen may also be formed either directly or by the catalysts, according to the equation $CO + H_2O = CO_2 + H_2$. It then acts as follows:— $CO + 3H_2 = CH_4 + H_2O$, $CO_2 + 4H_2 = CH_4 + 2H_2O$.

Lactonisation of α-Ketonic Ethers.—H. Gault.—When pyruvic acid is etherified by ethyl alcohol in presence of HCl, a complex mixture of ethers is obtained. These include ethyl pyruvate, the corresponding acetal, ketovalerolactone carbonic ether, and another lactone ether which is the principal product of the reaction. From the study of the derivatives which this compound forms with hydrazine hydrate and with ammonia the author has proved that it is the ethyl ether-oxide of ketovalerolactone carbonic ether (methylethoxyketodihydrofurfurane carbonic ether).

Action of Sodammonium on True Acetylenic Hydrocarbons.—Paul Lebeau and Marius Picon.—Sodammonium acts on the true acetylenic hydrocarbons of the fatty series to give the sodium derivatives of the hydrocarbons and the corresponding ethylenic hydrocarbon in the proportion of one molecule of the latter to two of the former. Thus with allylene the reaction is $3C_3H_4 + 2NH_3Na = 2C_3H_3Na + C_3H_6 + 2NH_3$. The products obtained in this reaction are very pure, and no secondary reactions have been observed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 10, 1913.

Fixation of Atmospheric Nitrogen by Boron Compounds.—Arthur Stähler and John Jacob Elbert.—The reduction of B_2O_3 by means of carbon begins at 1200°, and that of calcium borate (in presence of nitrogen) at 1280°. The yield of boron when fused borax is electrolysed amounts to 12·1 per cent. The authors have shown that calcium boride can probably be prepared from boron oxide and calcium carbide, and have proved that boron nitride begins to give up nitrogen at 2450°. 26—28 per cent of BN is obtained from boron oxide, carbon and nitrogen at 1500—1700°, and under ordinary pressure, while at higher pressures more than 85 per cent BN can be obtained. From boro calcite, carbon and nitrogen at 1800—1400° nearly the theoretical quantity, 46 per cent, of combined nitrogen can be obtained, an increase of pressure having no effect.

Antimony Pentachloride as a Reagent for Aromatic Hydrocarbons.—Siegfried Hilpert and Ludwig Wolf.—A mixture of 1 volume of antimony pentachloride and 2 volumes of carbon tetrachloride is a sensitive reagent for the detection of aromatic hydrocarbons. With pure benzene it gives a yellow or yellowish red coloration, while with commercial benzene the colour rapidly changes to dirty green, and after a time a dark precipitate is formed. Anthracene gives an intense green precipitate, and carbazol a lighter green precipitate. These colorations can be used to test the purity of anthraquinone. All hydrocarbons in which more than one phenyl group is linked to a carbon atom, such as diphenyl methane, triphenylmethane, fluorene, give green addition products, the colours of which are altered if other substituents are present. Thus methyl produces a red tinge, while a nitro-group lightens the colour to yellow or white.

Action of Calcium Hydride on Sulphates.—E. Ebler and K. Herrdegen.—When calcium hydride acts on barium sulphate the following reaction occurs:— $BaSO_4 + 4CaH_2 = BaS + 4CaO + 4H_2$. If 1 molecule of the sulphate to be reduced is mixed with 4 molecules of calcium hydride the reaction begins without any heating; in a few seconds the mass becomes white hot and the hydrogen generated catches fire and burns with a reddish flame. Many sulphates react with calcium hydride, those of heavy metals sometimes yielding the metal. Lead sulphate reacts with explosion.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [1.], No. 8, 1913.

Researches on Aromatic Ketones.—Luigi Alessandri.—When diazomethane acts on phenanthrene quinone gas is evolved, and finally an orange-yellow solution is obtained. From this orange crystalline needles, fusing at 167°, can be separated. Their formula is $C_{15}H_{10}O_2$, and they are formed by the addition of a molecule of methylene to a molecule of ketone, $C_{14}H_8O_2 + CH_2N_2 = C_{15}H_{10}O_2 + N_2$. The substance is stable towards permanganate. When it is boiled with an alcoholic solution of hydroxylamine it is partly converted into two products, the properties of which agree with those of the mono- and dioxime of phenanthrene quinone.

No. 9, 1913.

Influence of Halogens on Phototropism in Hydrazones.—F. Graziani.—The author has studied the phototropism of the hydrazones derived from the three isomeric chlorophenylhydrazines, and has found that none of the *o*-chlorophenylhydrazones prepared exhibits the phenomenon of phototropism. All of the seven meta-compounds are more or less phototropic, while of the eight para-compounds obtained four were phototropic.

Binary System of Chloride of Lithium with Chlorides of Alkaline Earth Metals.—C. Sandonnini.—Lithium chloride yields solid solutions with magnesium

chloride in all proportions; these solutions are stable at low temperatures. With calcium chloride it also gives solid solutions, which decompose on cooling. With the chlorides of barium and strontium it gives eutectics.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Birmingham Meeting of the British Association:—

President—Prof. W. P. Wynne, D.Sc., F.R.S.

Vice-Presidents—Prof. Adrian Brown, M.Sc., F.R.S.; Prof. P. Frankland, Ph.D., M.Sc., F.R.S.; Prof. A. Senier, M.D., Ph.D.; Prof. T. Turner; Mdme. Curie.

Secretaries—E. F. Armstrong, D.Sc., Ph.D. (Recorder); C. H. Desch, D.Sc., Ph.D.; A. Holt, D.Sc.; Hamilton McCombie, M.A., B.Sc., Ph.D.

Committee—Prof. H. E. Armstrong, F.R.S.; Prof. H. Bassett; Prof. P. P. Bedson; Dr. Beilby, F.R.S.; Prof. Bone, F.R.S.; Prof. J. B. Cohen, F.R.S.; Prof. H. B. Dixon, F.R.S.; Dr. J. V. Eyre; Mr. T. Fairley; Prof. A. Findlay; Mr. A. Fleck; Prof. F. Feist; Dr. T. M. Lowry; Dr. A. McKenzie; Dr. R. S. Morrell; Dr. R. H. Pickard; Prof. W. J. Pope, F.R.S.; Dr. T. S. Price; Dr. W. Rosenhain, F.R.S.; Dr. R. E. Slade; Mr. F. Soddy, F.R.S.; Dr. J. F. Thorpe, F.R.S.; Prof. L. Tchugaeff; Sir William A. Tilden, F.R.S.

The Papers brought before the Section were as follows:—

Prof. W. P. WYNNE, F.R.S.—Presidential Address.

Prof. J. B. COHEN, F.R.S., and P. K. DUTT—The Progressive Bromination of Toluene.

Dr. R. S. MORRELL—The Saturated Acids of Linseed Oil.

Dr. C. K. TINKLER—A Series of Mixtures of Nitro-compounds and Amines which are Coloured only in the Liquid State.

E. VANSTONE—Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.

Prof. W. M. THORNTON—The Influence of the Presence of Gas on the Inflammability of Coal-dust in Air.

H. EHRHARDT—Decomposition Products of Indigo in the Vat.

Reports of Research Committee—(*a*) Hydro-aromatic Substances. (*b*) Aromatic Nitroamines. (*c*) Dynamic Isomerism. (*d*) Plant Enzymes.

Dr. W. ROSENHAIN, F.R.S.—The Amorphous Phase in Metals (with discussion).

Prof. TURNER—The Volatilisation of Metals in a Vacuum.

O. F. HUDSON—The Structural Changes brought about in Certain Alloys by Annealing.

Dr. C. H. DESCH—Further Experiments on Diffusion in Solids.

F. E. E. LAMPLOUGH and J. T. SCOTT—Some Phenomena in the Formation of Eutectics.

Dr. A. HOLT—The Solution of Gases in Metals.

E. VANSTONE—The Electrical Conductivities of Sodium Amalgams.

F. D. FARROW—The System Copper—Oxygen.

R. E. SLADE and G. I. HIGSON—Equilibria of Reduction of Oxides by Carbon.

R. E. SLADE and G. I. HIGSON—The Dissociation Pressures of some Nitrides.

F. JOHNSON—A Study of the Degradation or Enhancement of Quality of Commercial Copper by the presence of Impurities.

Dr. R. H. PICKARD and J. KENYON—Optical Rotatory Powers and Dispersions of the Members of Homologous Series.

Dr. T. M. LOWRY—Rotatory Dispersion.

Dr. T. S. PATTERSON—(1) The Influence of Temperature and Solution on Rotation. (2) Some Suggestions Regarding the Nomenclature of Optical Activity.

Prof. L. TSCHUGAEFF—Anomalous Rotatory Dispersion.

Lieut.-Col. W. GIFFORD—A Partially Corrected Fluor-quartz Lens System for Spectrum Photography.

Dr. J. HULME—Crystalline-liquid Substances.

Dr. BEILBY, F.R.S.—Low Temperature Carbonisation.

Prof. W. A. BONE, F.R.S.—Gas Producers and the Use of Gas.

Dr. R. V. WHEELER—The Composition of Coal.

Dr. M. G. CHRISTIE—Coking and By-product Recovery from Small Coal.

Dr. H. G. COLMAN—The Manufacture of Coal-gas.

J. H. YATES—Gas Fires.

W. H. PATTERSON—The Improvement of Combustion and Blending of Coals.

Dr. R. LESSING—Smokeless Fuel and Coal Oil,, and their Relation to Smoke Abatement.

J. F. LIVERSEEGE and A. W. KNAPP—The Action of an Alkaline Natural Water on Lead.

Discussion on Radio-active Elements and the Periodic Law, opened by F. SODDY, F.R.S.

A. FLECK—The Chemistry of the Radio Elements.

Dr. G. HEVESY—Radio-active Elements as Indicators in Chemistry and Physics.

Dr. B. DE SZYSZKOWSKI—(1) Neutral Salt Action. (2) Solubility and Distribution.

Dr. PRIDEAUX—The Hydrogen Ion Concentration of the Sea and the Alkali Carbon Dioxide Equilibrium.

Prof. F. FRANCIS—A New Method for the Determination of Hydroxyl Ion Concentration.

Discussion on Prof. Bragg's Paper on X-Rays and Crystals.

Radio-active Constituents of Sediment of Thermal Springs at Hokuto, Taiwan.—Masataro Hayakawa and Tomonori Nakano.—It has already been observed that the sediment of the thermal springs at Hokuto is radio-active. The sediment consists chiefly of angleso-barytes, but it contains also small quantities (about 0·2 per cent) of cerium and lanthanum. At least three radio-active elements are present in it, viz., ionium, polonium, and radium. The mineral contains no uranium.—*Memoirs of the College of Science and Engineering*, Kyoto Imperial University, v., 4, 137.

Reactions of Ozone with certain Inorganic Salts.—Yoshito Yamauchi.—So far as the author, using a new method of determining the concentration of ozone, could ascertain, ozone is decomposed according to the equation $O_3 = 3O$ only in the case of the oxidation of stannous chloride. The decomposition usually occurs according to the equation $O_3 = O_2 + O$. When ozone acts on sodium thiosulphate two reactions take place, the ozone first causing the catalytic decomposition of the thiosulphate and then effecting the partial oxidation of the sulphite formed. Ozone very rapidly and completely gives thallic oxide with a thallous salt, and a gravimetric method of determining ozone may be based upon this fact.—*Memoirs of the College of Science and Engineering*, Kyoto Imperial University, v., 4, 151.

Proposed International Rubber Congress and Exhibition at Batavia (Java), September, 1914.—The object of the Congress, which will be held from September 7th to September 12th, is the study of the scientific, economical, technical, and commercial questions which concern the rubber culture and industry. Well-known authorities will be invited to contribute dissertations, and the subjects which are best suited for the purpose will, after they have been reported upon, be brought into debate during the Congress. The Secretary of the Committee, Dr. C. J. J. van Hall, Buitenzorg (Java), will willingly supply any information desired concerning the Congress, a definite programme of which will shortly be issued. The Exhibition will be open from September 8th to October 14th, 1914, and will show how the culture and preparation of rubber is conducted in the principal producing countries. Manufactured rubber goods will also be exhibited and sold. Applications for space should be made before November 1st, 1913, to the Secretary General of the International Rubber Congress and Exhibition, Batavia, 1914, Weltevreden (Java), to whom all correspondence concerning the Exhibition should be addressed.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2810.

THE STRUCTURAL CHANGES BROUGHT ABOUT IN CERTAIN ALLOYS BY ANNEALING.*

By O. F. HUDSON, M.Sc., A.R.C.S.

A large number of the useful alloys, particularly those which are rolled, drawn, or otherwise worked, consist of crystals of one kind only—viz., a solid solution. When alloys of this class are annealed, the structural changes that may be observed are: —

1. The cored structure usually characteristic of the alloy in the cast state gradually disappears, and the crystals become quite uniform in composition throughout. Structurally the alloy does not now differ from a pure metal, and other structural changes due to annealing are similar in both cases.

2. If the alloy has been worked before it is annealed pronounced crystal growth is observed when the annealing takes place above a certain temperature, which varies with the alloy. In most cases also numerous twinned crystals are seen. In effect the alloy is recrystallised. If the temperature of annealing is raised the crystal growth becomes more pronounced, particularly from certain centres, and a very coarsely crystalline (overheated) metal or alloy may result. It is, however, to be noted that if the annealing is carried out at a suitable temperature a finer structure than the original is obtained.

The recrystallisation of the strained alloy and the disappearance of the "cores" go on side by side until uniformity of composition is reached.

In the case of alloys consisting of crystals of two or more kinds, those which are malleable are usually composed of crystals of two solid solutions. Generally the chief effect of annealing these alloys is to promote equilibrium between the two phases present. Crystal growth also takes place partly on lines similar to those indicated above and partly by the absorption of the smaller crystals in larger ones of the same kind. In some cases the annealing operation may result in a true recrystallisation. Complete phase and structural equilibrium in some alloys of this class are only attained after very prolonged annealing, and in many instances the alloys as used are in a metastable condition.

The decrease in hardness and the lowering of the elastic limit due to the annealing of cold worked metals and alloys are almost complete before crystal growth becomes noticeable, and are apparently unaccompanied by structural changes which can be observed by microscopical examination.

DIFFUSION IN SOLID SOLUTIONS.*

By CECIL H. DESCH, D.Sc., Ph.D.

Since the author's report to the Dundee Meeting of the Association, Bruni and Meneghini have succeeded in demonstrating the occurrence of diffusion in a clear crystalline solid in the case of sodium and potassium chlorides. A mixture of these two salts, heated at 500° or 600°, yields a homogeneous solid solution, the formation of which is recognised by determining the heat of solution in water, which differs from that of a mechanical mixture.

The author's further experiments with metallic alloys show that a sharp boundary is characteristic of diffusion in solids when a chemical compound is formed. An abrupt discontinuity of composition is also observed when one component is removed by solution, as in the dezincification of alloys of copper and zinc.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

THE VOLATILITY OF METALS.*

By Prof. T. TURNER, M.Sc.

Considerable attention has been devoted during the past few years to the volatility of metals, especially *in vacuo* or under reduced pressure, and there are considerable possibilities of practical applications in this direction in future. The boiling-points of metals under various conditions as to pressure and atmosphere have been determined by Greenwood and by Kraft, while Berry, Groves, Wait, and the author have investigated the behaviour of metals and of alloys *in vacuo*. Distillation *in vacuo* is specially suitable for volatile and easily oxidisable metals such as sodium, potassium, cadmium, and zinc; lead and bismuth can also be dealt with by similar means. When alloys are heated to suitable temperatures *in vacuo* in certain cases quantitative separation can be readily effected as with the zinc copper, zinc-iron, and tin-lead series. In other cases, as with the copper-nickel, copper-tin, and copper-iron series, neither metal appreciably volatilises. In some instances definite chemical compounds are obtained. The rate of volatilisation is very markedly affected by the pressure, and to some extent also by the nature of the atmosphere employed. A certain definite or critical temperature is required in order to obtain appreciable volatilisation, and this temperature is raised by gaseous pressure. When this critical temperature has been reached the rate is independent of the initial pressure or the nature of the gas, but varies directly as the increase of pressure. In other words, if the initial rate be R and the rate at any higher temperature to R', then $R' = R + at$. There is an abrupt change in the direction of the temperature curve for equal rates of volatilisation when the pressure reaches 50 mm. of mercury; and at above 80 mm. the curve becomes a straight line. On exhausting it is found that the removal of 1 mm. at from, say, 2 to 1 mm. pressure produces approximately seventy times the effect of the removal of 1 mm. when starting from any pressure above 50 mm.

OPTICAL ROTATORY POWERS AND DISPERSIONS OF THE MEMBERS OF SOME NEW HOMOLOGOUS SERIES.*

By R. H. PICKARD and J. KENYON.

The authors have synthesised the optically active forms of over 100 compounds belonging to the following ten series:—(1) Methyl alkyl carbinols, Me.CHOH.R, (2) esters of methyl ethyl carbinol and normal fatty acids, MeEt.CH.O.COR, (3) esters of methyl *n*-butyl carbinol $Me(C_4H_9)CH.O.COR$, (4) esters of methyl *n*-amyl carbinol $Me(C_5H_{11})CH.O.COR$, (5) esters of methyl *n*-hexyl carbinol $Me(C_6H_{13})CH.O.COR$, (6) esters of methyl *n*-nonyl carbinol $Me(C_9H_{19})CH.O.COR$, (7) acetates of methyl *n*-alkyl carbinols $Me.R.CH.O.COCH_3$, (8) *n*-dodecoates of the same $Me.R.CH.O.COC_{11}H_{23}$, (9) ethyl alkyl carbinols Et.CHOH.R, (10) *iso*propyl alkyl carbinols $Me_2CHOH.R$. (In each series the "growing chain" is normal and not branched.)

All these compounds possess simple and closely related constitutions, but no numerical relationship between their rotatory powers has as yet been detected. The optical rotatory and dispersive powers of the compounds show well-marked regularities, which are more or less common to all the series. The most pronounced of these is that due to the special stereochemical configuration of that member of an homologous series in which the growing chain (R or —COR in the above formulæ) contains five carbon atoms.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

DYNAMIC ISOMERISM.*

A. *Rotatory Dispersion.*

THE past year has witnessed the culmination of an investigation that has a close relationship to the main line of research for which the Committee is responsible. The marked progress that has been made in the study of rotatory dispersion may be shown by the list of papers which have been published during the year. These include a paper on—

"Optical Rotatory Dispersion." Part I. "The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum" (*Phil. Trans.*, 1912, A, ccxii., 261—97),

which will be followed shortly by Part II., in which the extension of the polarimetric method through the ultra-violet and infra-red regions of the spectrum will be described.

The application of these new physical methods to the study of chemical problems is described in a second series of papers, of which the following have been published already, or are in preparation ready for publication in the autumn :—

"The Rotatory Dispersive Power of Organic Compounds."

I. "The Measurement of Rotatory Dispersion" (*Trans. Chem. Soc.*, 1913, ciii., 1062—1067).

II. "The Form of the Rotatory Dispersion Curves" (*Trans. Chem. Soc.*, 1913, ciii., 1067—1075).

III. "The Measurement of Magnetic Rotatory Dispersion" (*Trans. Chem. Soc.*, 1913, ciii., 1322—1331).

IV. "Magnetic Rotation and Dispersion in some Simple Organic Liquids" (*Proc. Chem. Soc.*, June 19, 1913).

V. "A Comparison of the Optical and Magnetic Rotatory Dispersion in some Simple Organic Liquids."

VI. "Anomalous Rotatory Dispersion" (*Proc. Chem. Soc.*, June 5, 1913).

Attention may also be directed to a paper by Armstrong and Walker on "The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power" (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388—403), in which the close relationship between rotatory dispersion and dynamic isomerism is specially emphasised.

The general result of these investigations has been to show that a knowledge of the phenomena of dynamic isomerism is essential for the interpretation of optical rotation, especially in the case of liquids which show anomalous rotatory dispersion; conversely, it is believed that the study of rotatory dispersion will open up a new and fruitful field for the investigation of dynamic isomerism in the case of large groups of important compounds.

B. *Successive Isomeric Changes.*

The past year has also seen the completion of a long series of experiments on the complex isomeric changes which take place in the amide and piperidide of camphorcarboxylic acid. Nearly five years ago it was discovered that these substances were capable of giving inflected mutarotation curves. An investigation of "The Equations for Two Consecutive Unimolecular Changes" (Lowry and John, *Trans. Chem. Soc.*, 1910, xcvii., 2634—2645) showed that inflected curves might be produced by two successive isomeric changes, but the experimental curves were found to be more complex, giving indications of at least three successive changes involving four isomeric compounds. These experiments have been described in detail in two papers published during the past year (Glover and Lowry, *Trans. Chem. Soc.*, 1912, ci., 1902—1912; 1913, ciii., 913—924).

Experiments are now in progress with a view to investigating Forster's α-benzoyl camphor, the enolic form of which has been found to give inflected mutarotation curves when ethylene chloride is used as a solvent in place of chloroform. Even nitrocamphor has been found to give inflected curves if dissolved in ethylene chloride or in benzene (Lowry and Courtman, *Trans. Chem. Soc.*, 1913, ciii., 1216), but it is believed that these are due to the gradual absorption of a catalyst from the walls of the polarimeter tube, and not to successive isomeric changes.

C. *Influence of Light.*

A series of experiments on the influence of light on isomeric change (Lowry and Courtman, *Trans. Chem. Soc.*, 1913, ciii., 1214—1221) has shown that no marked acceleration is produced by exposing nitrocamphor, glucose, galactose, or maltose to the action of powerful ultra-violet light. In the case of aminomethylene camphor, however, very marked acceleration occurs whilst the light is acting, but the action reverts to its original slow rate of change when the light is withdrawn. In the case of (enolic) α-benzoyl camphor a similar acceleration is produced, but the effect continues after the light has been extinguished; it is believed that this permanent stimulation of the action is due to the liberation of benzoic acid acting as a catalytic agent.

* Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Dr. J. J Dobbie, and Dr. M. O. Forster. (Drawn up by the Secretary). Read before the British Association (Section B), Birmingham Meeting, 1913.

THE ELECTRICAL CONDUCTIVITIES OF SODIUM AMALGAMS.*

By ERNEST VANSTONE, M.Sc.

CONTINUING the physico-chemical investigation of sodium amalgams, the author has determined their electrical conductivities when in the solid state. The amalgams were melted and drawn up into a capillary spiral 1 mm. diameter, and about a metre in length when unwound. Platinum terminals were sealed in at each end of the spiral.

The liquid amalgam in the spiral was allowed to cool slowly and to solidify in the capillary tube, care being taken to preserve the continuity and uniformity of the thread.

The resistance was measured by a potentiometer method. About twenty amalgams have been examined, the composition varying from 0 to 45 atoms per cent of mercury.

The resistances varied from 0·05 to 0·4 ohm, and the specific conductivities from 18×10^{-4} to $1\cdot9\times10^{-4}$. The resistances were measured at a temperature of 15° C. The curve obtained by plotting specific conductivies as ordinates and atomic percentages as abscissæ shows two discontinuities and a minimum point. The breaks occur at 85·5 and 77·9 atoms per cent of sodium, and the minimum point at 65 per cent sodium. The thermal diagram has breaks at 85·2, 71·7, and 63·3 per cent sodium.

* Read before the British Association (Section B), Birmingham Meeting, 1913).

EQUILIBRIA OF REDUCTION OF OXIDES BY CARBON.*

By R. E. SLADE and G. I. HIGSON.

THE equilibrium pressures obtained when certain oxides are reduced by carbon have been determined.

The reaction which takes place is of the type—

$$MO+C \rightleftharpoons CO+M$$

where M denotes two equivalents of one of the following substances :—V, Ta, Cr, B, Mn, Sn.

In some cases a carbide is formed. This reaction is represented by the equation—

$$2MO + 3C \rightleftharpoons M_2C + 2CO.$$

In the experimental method employed there was always an excess of the free metal present. In either case there are three components, M, C, and O, and four phases, CO, M, MO, and either C or M_2C. Therefore, there is one degree of freedom of the system. At each temperature there is a definite pressure of CO.

The substance M was heated in an unglazed porcelain boat *in vacuo*, in the furnace already described by one of us (*Proc. Roy. Soc.*, 1912, lxxxvii., A, p. 519). CO was admitted and reacted with the substance until the pressure had fallen to that of equilibrium. Some CO was then pumped out and the equilibrium attained from the other side.

The upper limit of temperature in some cases was determined by the volatility of the metal, the lower limit of temperature is 800—900° when the reaction—

$$2CO \rightleftharpoons CO_2 + C$$

begins to take place to some extent. Summary of experimental results :—

	Temperature.	Pressure.
Vanadium	1340°	1·5 mm.
Tantalum	1270°	<0·1 mm.
Chromium	1292°	6·2 mm.
.. .. ..	1339°	9·2 mm.
Tin	750°	>760 mm.
Tin in presence of SiO_3	753°	670 mm.

The values of the equilibrium pressures have also been calculated on the basis of the Nernst heat theorem, and the heats of reaction calculated from the equilibrium pressures when the heats of reaction were not previously known.

THE SYSTEM COPPER-OXYGEN.*

By F. D. FARROW.

This paper presented in a concise form the results of the work on the melting-points and dissociation pressures of the system copper-oxygen, obtained by Heyn, Wöhler, and by Slade and Farrow. Heyn has obtained melting-points of mixtures containing up to 1 per cent of oxygen. He finds a eutectic point with an oxygen content of 0·39 per cent at 1065° C., while the mixture containing 1 per cent of oxygen melts at 1167° C.

Slade and Farrow have shown that mixtures containing between about 2·3 and 10·3 per cent of oxygen when heated above 1195° C. melt and form two liquid layers, the upper of which is richer in oxygen than the lower. The composition of these layers is for all temperatures investigated about 2·3 per cent of oxygen for the lower and about 10·3 per cent for the upper. The compositions do not appear to approach each other with rising temperature. By extrapolating over a short distance the authors place the melting-point of cuprous oxide (11·26 per cent of O) at 1210° C.

The same authors have investigated systems whose composition lies between those of cuprous and of cupric oxide. They find two melting-point curves which intersect at about 1060° C. The eutectic mixture corresponding to this has a composition of 14·8 per cent of oxygen. The melting-point of cupric oxide is found not to have been attained at a temperature of 1148° C., at which temperature the dissociation pressure of the oxide exceeds 2½ atmospheres.

Wöhler has determined the dissociation pressures of cupric oxide when heated. He has shown that solid solutions of cuprous oxide in cupric oxide are formed. His values therefore are somewhat lower than the highest dissociation pressures obtainable.

Slade and Farrow have determined the dissociation pressures of cuprous oxide at temperatures and under conditions at which the mixture of two liquid phases mentioned above must necessarily have been present. These pressures are given in the subjoined table as points on the experimental curve *c g*.

From the sources mentioned the data have been collected and used to construct a temperature-composition and a temperature-pressure diagram which are attached to the paper.

Table of Numerical Values of the Data Represented by the Chief Points on the Diagrams.

Name.	Temperature Centigrade.	Composition =oxygen content per cent.	Pressure.
a	1084	0·0	—
b	1065	0·39	—
c	1195	2·26	—
d	1210	11·16	—
e	*c.* 1060	*c.* 14·8	*c.* 460 mm.
f	?*c.* 1240	20·10	? 20 atm.
Curves.			
m e	960	—	50 mm.
	1050	—	314 mm.
	1070	—	458 mm.
c g	1205	—	4 mm.
	1240	—	10 mm.
	1260	—	12 mm.
	1324	—	25 mm.

Explanation.

(*a*) Melting-point of pure Cu.
(*b*) Cu, Cu_2O eutectic.
(*c*) Invariant point. Phases present : Solid Cu_2O, liquid I. Liquid II. Gas.
(*d*) Melting-point of pure Cu_2O.
(*e*) Cu_2O, CuO eutectic.
(*f*) Melting-point pure CuO.
(*m e*) Wöhler's curve of CuO dissociation pressure.
(*c g*) Slade *v.* Farrow's curve of dissociation pressure of the two liquid phases of the Cu_2O, Cu mixture.

* A Paper read before the British Association (Section B), Birmingham Meeting, 1913.

A STUDY OF THE

DEGRADATION OR ENHANCEMENT OF QUALITY OF COMMERCIAL COPPER BY THE PRESENCE OF IMPURITIES.*

By FREDERICK JOHNSON, M.Sc.

In this paper the author surveyed the facts and theories which have been brought to light of late years by modern scientific investigation of the influence of traces of impurities upon the chemical, physical, and mechanical properties of copper. Much of the mystery formerly attaching to defects during manufacture and failures in service has been cleared up, to the benefit alike of the manufacturer and the user. Ancient and modern prejudice against the presence of impurities such as oxygen and arsenic has been shown to have no foundation in fact when certain uses of the copper are considered.

The knowledge of metallurgical testing and analysis was shown to be indispensable when the varying composition of commercial brands of crude copper and the multitudinous uses to which refined copper is put are taken into consideration.

Manufacturers should never lose sight of such fundamental considerations as the following :—

* Read before the British Association (Section B), Birmingham Meeting, 1913.

1. To what degree the various impurities may be eliminated during refining operations.

2. To what specifications (however imperfect such specifications may be) the resulting changes may have to conform.

3. To what extent impurities may mutually react to the improvement or detriment of the resulting material.

The author has given special attention to the influences of oxygen and arsenic, whilst bismuth, lead, nickel, antimony, silicon, iron, phosphorus, manganese, &c., are all dealt with in turn.

The evidence of the microscope is called largely into requisition and the importance of various kinds of testing is emphasised.

THE DISSOCIATION PRESSURES OF SOME NITRIDES.*

By R. E. SLADE and G. I. HIGSON.

THE dissociation pressures of the nitrides of vanadium, tantalum, and boron have been investigated.

The substance was heated in an unglazed porcelain boat *in vacuo*, in the furnace previously described by one of us (*Proc. Roy. Soc.*, 1912, lxxxvii., A, p. 519). Nitrogen was admitted and was absorbed by the substance to form nitride until the dissociation pressure was attained. Some nitrogen was then pumped off and the equilibrium attained from the other side.

Summary of experimental results:—

	Temperature.	Pressure.
Vanadium ..	1203°	Not greater than 0·2 mm.
..	1271°	Not greater than 1·5 mm.
Tantalum ..	1170°	0·4 mm.
Boron	1222°	Not greater than 9·4 mm.

The results are discussed from the point of view of the Nernst heat theorem.

ROTATORY DISPERSION.*

By T. MARTIN LOWRY, D.Sc.

ATTENTION was directed to the importance of making measurements of optical rotation over a range of wavelengths, instead of merely with light of one colour. This is specially necessary in the case of substances, such as derivatives of tartaric acid, in which anomalous rotatory dispersion is known or may be suspected to exist.

After experiments extending over a period or seven years, the methods of measuring rotatory dispersion have been so simplified that they are now within the range of the ordinary advanced student, and should soon become a regular part of the ordinary routine of the laboratory. For many purposes it is sufficient to take readings with the green and violet mercury lines, but sodium and lithium may also be used in order to see whether the curve of rotatory dispersion has the normal form. A still more valuable check is provided by readings taken with the red and green cadmium lines, but these require more complex apparatus and cannot yet be regarded as generally available.

The examination of the optical and magnetic rotatory dispersion of some fifty organic liquids has shown that the curve of rotatory dispersion has an extremely simple form. It can be expressed by the equation

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

where k is the "rotation constant" and λ_0^2 the "dispersion constant" for the substance. If α is plotted against λ_0^2 the curve is a simple rectangular hyperbola, tending to a limiting value $\alpha = 0$ when $\lambda^2 = \infty$ and to $\alpha = \infty$ when $\lambda^2 = \lambda_0^2$. If $\frac{1}{\alpha}$ is plotted against λ^2 the curve becomes a straight line. In the case of substances, such as ethyl tartrate, which show anomalous rotatory dispersion, two of these terms must be employed thus:—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}$$

This is in accordance with Biot's view that anomalous rotatory dispersion is produced by the admixture of two substances differing in rotatory dispersive power as well as in the sign of their optical rotations.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

ON ANOMALOUS ROTATORY DISPERSION.*

By L. TSCHUGAEFF.

1. THERE are three different types of anomalous rotatory dispersion. The anomaly in question may be due: (*a*) To the superposition of two (or more) different kinds of normally dispersing molecules, differing in rotatory dispersive power as well as in the sign of their rotation. This type of anomalous dispersion was first established by Biot. (Ex. mixture of *l*-menthone and *iso*-menthone.) (*b*) To the existence of absorption bands in the spectrum of the active substance, as it has been pointed out by Cotton, Drude, and others. (Cotton's phenomenon.) (Ex. the xanthates and thiourethanes of menthol, borneol, and fenchol.) (*c*) To the *intramolecular* superposition of partial rotations corresponding to several centres of activity of one and the same molecule, as it has been shown first by the author. Experimental evidence in favour of this classification is given.

2. It has been established that the shape of the dispersion curve is largely influenced by constitutive factors, and in the first place by the relative position of the centres of activity and of the chromophor groups within the active molecule, the whole dispersion curve resulting from the superposition of several "partial" curves. These results are discussed from the point of view of the electronic theory.

3. The influence of the temperature and the nature of the solvent on the rotatory dispersion of the optically active xanthates resembles closely the influence exerted by the same factors on the dispersion of tartaric acid and of its ethereal salts as studied by Winther and others. There must therefore be an intimate analogy in the origin of the anomaly in both cases.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

RADIO-ELEMENTS AS INDICATORS IN CHEMISTRY AND PHYSICS.*

By G. HEVESY, Ph.D.

BY means of an α-ray electroscope of ordinary sensitiveness it is possible to measure accurately as small a quantity as 10^{-17} grms. of a radio-active substance having a half-value period of one hour. The extraordinary simplicity and at the same time sensitiveness with which it is possible to measure these extremely small quantities of radio-active bodies makes them of the greatest use not only in studying substances in great dilution but also as indicators of physical and chemical processes.

Radio-active indicators may be conveniently divided into two principal groups. To the first group belong those whose use as indicators depends only on their physical properties and not on their chemical properties. Some

examples of the use of radio-active indicators of this kind are the following :—

It is only necessary to know that the radio-elements composing the active deposits are metals in order to test the formula of Arrhenius connecting the variation of velocity of solution of metals in acids with the temperature. This has been lately carried out by Miss Ramstedt.

It is known from the kinetic theory that the concentration of a solution varies with time, and this problem, which could not be attacked by ordinary methods, has been made experimentally feasible by the use of radio-active bodies as indicators. (Svedberg, Smoluchowski).

The existence of colloidal solutions of radio elements has been lately established by Paneth and Godlewski, and experiments have been undertaken on the formation and precipitation of these colloids using radio-active indicators.

The emanations, the only gaseous radio-elements, have been employed to establish the validity of the gas laws, especially that of Henry's law for extremely small partial pressures. (Bruhat, Boyle).

Fick's Diffusion Law has also been shown to hold accurately for bodies in infinitely small concentration by making use of radio-active substances.

It is often a question of practical interest to the chemist to know how often it is necessary to wash out a pipette or a beaker in order to remove the last trace of the solution it had contained. This problem can be investigated with extreme ease when radio-active indicators are used.

The fact, however, that most radio-elements are throughout in all chemical properties exactly similar to some of the common elements (for instance, radium D and thorium B are non-separable from lead, thorium C and radium E from bismuth, &c.) allows these bodies to be used chemically as indicators of the bodies from which they are known to be non-separable. Radium E can be used as an indicator for bismuth, radium D for lead, &c.

If 1 mgrm. of lead is mixed with a quantity of radium D which gives 10,000 units of activity in an electroscope, one-millionth part of this mixture is easily detectable by the radio-activity of radium D. In this way 10^{-6} mgrms. lead is quantitatively determinable.

By this method also the solubility of the difficultly soluble salts of lead, such as the chromate and the sulphide, has been determined. Further, the amount of lead chloride entrained by a precipitate of silver chloride after washing the latter thoroughly with water is measurable.

Experiments on the electrochemical behaviour of small quantities of lead and bismuth have been begun. By means of these indicators a study may be made of the electrochemical behaviour of these metals for electrode potentials lying below the decomposition voltage, a problem which could not be investigated by any other means.

Of especial use are the indicators for investigating the diffusion and mobility of ions in extremely small concentration, from which results we obtain information concerning the behaviour and the hydration of ions in very dilute concentration. Data are already available on the diffusion rate of lead salts down to a normality of 10^{-14}.

THE

ROTATION OF ACTIVE COMPOUNDS AS MODIFIED BY TEMPERATURE, COLOUR OF LIGHT, AND SOLUTION IN INDIFFERENT LIQUIDS.*

By T. S. PATTERSON, D.Sc. Ph.D.

Before it can be possible to offer a real explanation of the phenomena of optical activity, attention must be devoted to the lowlier task of trying to understand clearly the main features of the phenomena in question ; to study carefully, in fact, what may be termed the morphology of the subject. The variation of rotation with change in the colour o light, with change of solvent, with change of temperature, and perhaps even with change of pressure, must be thoroughly examined.

As regards the last little can be said, but the other three —colour of light used, the nature of the solvent, and the temperature—are of the utmost importance. Even the data available at present seem sufficient to give some idea of the general behaviour of optically active compounds with changes of condition, and this may be summed up into one scheme, as follows : —

It has been found that the rotation of certain active compounds reaches a maximum value at a certain definite temperature. Further, points of inflection often occur in temperature-rotation curves, sometimes in such as show also a maximum, and by piecing together the evidence collected from an examination of a fair number of optically active substances it seems probable that the variation of the rotation of an active substance with change of temperature may be, and very probably is, a periodic phenomenon, doubtless irregularly periodic—such that several maxima and minima may be expected to occur in the curve representing it. Owing to experimental difficulties, however, it is not possible to trace these curves through any very wide range of temperature.

Now it seems legitimate to assume that a point of maximum rotation indicates that condition of the substance in which one of the groups attached to the asymmetric atom attains to a maximum influence—a singular condition of the substance. When such singular points are found in the curves of condition for a number of fairly closely related compounds it seems reasonable to suppose that the maxima represent the rotations of these different compounds in, at least, fairly similar conditions. The great merit of a maximum rotation is its recognisability and the possibility it affords of tracing some particular state of the compound as the external conditions are varied. Maxima are found at different temperatures for the various members of a homologous series, but the discussion of this field, since it involves the relationship between the rotation and the constitution of a series of active compounds, may be passed over until the variation of rotation of a single active compound with change of external conditions is more fully understood.

Here the first matter to which attention may be directed is that the maximum, in certain cases at any rate, occurs at a different temperature for light of various refrangibilities, whence it would appear that the irregularly periodic temperature-rotation curves are probably retarded on each other ; and since the curve for violet light has the greatest amplitude, it follows that these curves cut one another throughout a certain region, and in this region the rotation-dispersion of the substance must necessarily be anomalous. Hence we arrive at once, not, it is true, at an explanation of anomalous rotation-dispersion, but at a reason why anomalous rotation-dispersion should exist at all.

It is doubtful whether any substance will really show normal rotation-dispersion, but if such a substance be found then it seems probable that the temperature-rotation curves for the different colours of light will intersect at a single point, the rotation-dispersion being positive on one side of this point and negative on the other.

Rotation in Solution.—A study of such data as are available appears to show that when such a compound as shows a maximum rotation—for example, ethyl tartrate—is dissolved in some indifferent liquid, this maximum rotation is displaced towards a lower or a higher temperature, as the case may be, with a corresponding alteration in value, solvents differing very much in regard to the displacement which they bring about. Now it is also found that the region in which abnormal rotation-dispersion takes place is shifted, on solution, in a very similar way to that in which the maximum rotation is displaced, and therefore it seems clear that the effect of solution is to displace the whole temperature-rotation curve. It then appears at once why some substances which show abnormal rotation-dis-

* Read before the British Association (Section B), Birmingham Meeting, 1913.

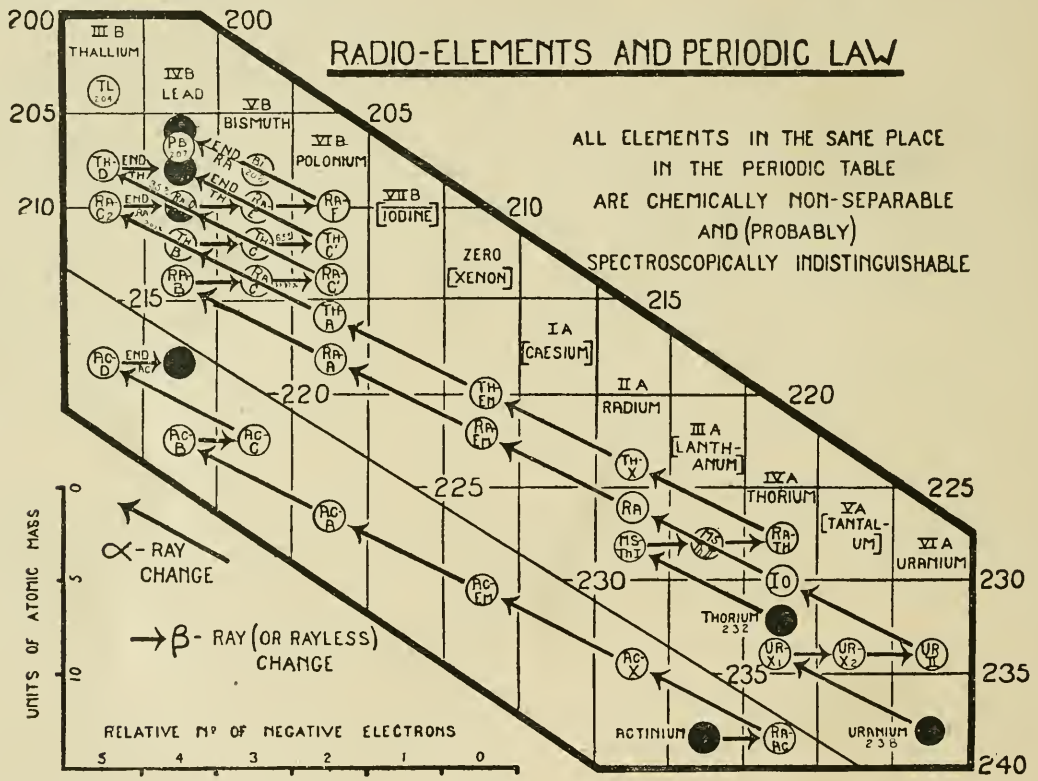
persion at a certain temperature for the homogeneous compound show a normal rotation-dispersion when dissolved in some solvent which considerably alters the rotation. The solvent has the effect of shifting the family of temperature-rotation curves in such a manner as to bring the parts of the curves in the neighbourhood of the maximum into view, and in this neighbourhood the rotation-dispersion appears to be normal.

THE RADIO-ELEMENTS AND THE PERIODIC LAW.*

By FREDERICK SODDY, M.A., F.R.S.

DURING the present year, 1913, the general law governing the passage through the periodic table of the elements in process of radio-active change has been discovered. As the result it is possible to write the three disintegration series of uranium, thorium, and actinium across the periodic table, so that each member falls into its proper place in the case of the twenty-seven members the chemistry of which is known. For the six members the period of average life of which is too short for the chemical nature to be determinable, and for the five inactive end-products, the chemical nature can be without uncertainty predicted. The general law is that an α-ray change, when a helium atom carrying two atomic charges of positive electricity is expelled, the element changes its place in the periodic table in the direction of diminishing mass and diminishing group number by two places. In a β-ray change, when a single atomic charge of negative electricity is expelled from the atom as a β-particle, and also in the two changes for which the expulsion of rays has not yet been detected, the element changes its position in the table in the opposite direction by one place.

The generalisation as regards the α-rays was put forward in 1911 (Soddy, "Chemistry of the Radio-Elements," p. 29), but at that time the chemistry of the β-rays giving members, which are mostly short-lived, was not known well enough for anything definite to be said. Fleck in 1911 commenced to make a systematic investigation of the chemically indefinite members, from the point of view adopted in the book referred to, of the existence of chemically identical and non-separable groups of elements. This work occupied two years. Some of the results were communicated to this section at the Dundee Meeting last year, and they have now been published in the Journal of the Chemical Society (*Proc.*, 1913, xxix., pp. 7, 172; *Trans.*, 1913, ciii., pp. 381, 1052). It is important to note that this work was purely experimental, and was done deliberately without any attempt to find the theoretical law, in order that the results might be free from all bias in favour of any particular view. It would have been easier to speculate first and then to test the speculations, but the opposite course was purposely adopted.



Fleck, in addition to confirming the chemical nature of several of the chemically better known members by careful fractionation methods, had by the beginning of this year succeeded in elucidating the chemical nature of nine members which had not previously been elucidated. All except two of these were in the series subsequent to the zero or emanation group, of which members only the two longest lived—polonium and radio lead—had previously been chemically characterised. At this time A. S. Russell (CHEM. NEWS, January 31, 1913, cvii., 49), who knew of Fleck's results, put forward the view that in the β-ray change the position of the element in the periodic table changes by one place, and he was the first to publish a complete scheme showing the passage of the radio-elements through the periodic table. His scheme was in

* Abstract of Paper opening the Discussion. British Association, Birmingham Meeting (Section B).

certain respects imperfect, and it was followed almost immediately by another by K. Fajans (*Phys. Zeit.*, February 15, 1913, xiv., pp. 131, 136), who put forward the complete law in its present form, and made important and accurate deductions as to the positions occupied by the still unplaced members. Soddy independently arrived at a complete scheme similar to that of Fajans (Chem. News, February 28, 1913, cvii., 97), but which in one respect possibly went somewhat further in regard to the generalisation that all elements falling into the same place in the periodic table are not merely similar in chemical properties, but are chemically identical, non-separable by chemical methods, and probably spectroscopically indistinguishable. From this the definite prediction was made that radium-C_2, thorium D, and actinium-D would prove to be non-separable from thallium, and radium A from polonium, which Fleck has since established, whilst all the end-products would be non-separable from lead. The scheme, altered slightly to bring it up to date (July, 1913), is shown in the accompanying plate.

In all three schemes a new member was indicated in the V.A family, as the product of uranium X. This has since been discovered by Fajans and Beer (*Naturwissenschaften*, April 4, 1913), and confirmed by Fleck (*Phil. Mag.*). It proves to be a very short-lived substance of period of average life 1·7 minutes, and is called Uranium X_2. Its parent, Uranium X_1, with period 35·5 days, gives only the soft (β) rays, whereas the hard β-rays of uranium X come from this new product.

This missing member being short-lived disproves the suggestion (Soddy) that it might be a very long-lived and and therefore well-defined element (Eka tantalum), disintegrating dually, and producing, in addition to uranium II. by a β-ray change, actinium by a still undetected α-ray change. This being disproved, the only other possibility to consider as to the still unknown source of actinium is that it is produced in a β-ray or rayless change from radium. On account of the uncertainty of the origin of actinium, and therefore of the atomic weight both of itself and of all its products, the actinium series is shown separately beneath the others in the plate.

The chemical analysis of matter is thus not an ultimate one. It has appeared ultimate hitherto, on account of the impossibility of distinguishing between elements which are chemically identical and non-separable unless these are in the process of change the one into the other. But in that part of the Periodic Table in which the evolution of the elements is still proceeding, each place is seen to be occupied not by one element, but on the average, for the places occupied at all, by no less than four, the atomic weights of which vary over as much as eight units. It is impossible to believe that the same may not be true for the rest of the table, and that each known element may be a group of non separable elements occupying the same place, the atomic weight not being a real constant, but a mean value, of much less fundamental interest than has been hitherto supposed. Although these advances show that matter is even more complex than chemical analysis alone has been able to reveal, they indicate at the same time that the problem of atomic constitution may be more simple than has been supposed from the lack of simple numerical relations between the atomic weights.

Hydrolysis of Levulosanes.—Ph. L. de Vilmorin and F. Levallois.—In the hydrolysis of inulin sulphuric and oxalic acids gives results which are too variable to serve as a basis for a method of analysis. Acetic acid used at a temperature of about 80° and a concentration of 3 to 10 per cent is accurate, but as the temperature is raised the results obtained become rather too high. Very small quantities (0·72 to 4·3 grms. per litre) of sulphosalicylic acid at temperatures varying from 80° to 100° give accurate results.—*Bull. Soc. Chim. de France*, xiii.-xiv., No. 13.

ON THE

CRYSTALLINE DEPOSIT OCCURRING IN THE TIMBER OF THE "COLONIAL BEECH" (*Gmelina Leichhardtii*, F.v.M.).*

By HENRY G. SMITH, F.C.S.

This Australian tree belongs to the Family Verbenaceæ, and is thus not a true "beech." The use of this common name for *Gmelina Leichhardtii* is an unfortunate one, as it really belongs to the genus *Fagus* of the Cupuliferæ. The tree is a native of New South Wales and Queensland, and grows to a considerable size, reaching to a height of 100 to 150 feet, with a diameter of over 3 feet. It is a useful commercial timber, light in colour, but with little or no figure, and thus cannot be classed as ornamental, although it is useful for carving and similar art purposes.

The seasoned timber often has white particles filling the cells of the wood, and these are sometimes so plentifully distributed that the planed surface has the appearance of having been filled, to a certain extent, with a substance like plaster-of-paris. When the timber is not sound this substance often accumulates in "shakes" and cracks of the wood as small opaque deposits, and in crystalline masses. Under the microscope these masses were seen to consist of needle crystals.

The presence of some substance in "beech," different from that of other native timbers, has previously been observed by saw-millers, and in a letter from Mr. W. Smith, of Tinnonee, New South Wales, he refers to this peculiarity as follows:—"Port Macquarie Beech contains something of a very cleansing nature. We have a planing machine, and, of course, it gets dirty, and stuck all over with sap and dust from tallow-wood and other hard woods, but as soon as we have put through a few beech boards, wherever the sappy chippings strike, the ironwork of the machine becomes clean and as bright as new."

Another saw-miller also mentioned that he had seen whitish deposits in "beech" timber, but thought them to be a fungoid growth.

The first well-defined deposit of this substance came into the possession of the Technological Museum a few years ago, and as much work as possible was, at that time, carried out with it, a crystalline body being isolated, and its melting-point determined. About two years later a small quantity was received from another locality, and similar crystals were again isolated from it, and found to be identical in appearance with the first, and to melt at the same temperature. Through the kindly assistance of Mr. Breckenridge, a Sydney timber merchant, a portion of a beech log in a very unsound condition was recently obtained from which a few grms. of pure crystals were extracted, sufficient to enable a more extended investigation to be undertaken.

The crystals obtained from all the trees from the various localities were colourless, odourless, and tasteless, and were identical in crystalline form, in melting-point, in optical activity, and exhibited the same peculiarity in the melting-points of the substance when in either the crystalline or the amorphous conditions. From this it is apparent that the deposit is a common constituent in the timber of this species of *Gmelina*, and also that it is a definite chemical substance. It is possible that it may be characteristic of this tree, or perhaps peculiar to the genus, and if so, its identification would become of some assistance towards correct diagnosis, especially as no other body appears to be present in the deposit which might contaminate it, and thus interfere with the ready isolation and purification of the crystals.

The peculiarity of this body in what appears to be perhaps an example of dynamic isomorphism in a natural chemical

* A Paper read before the Royal Society of New South Wales, November 6, 1912. From the *Journal of the R. S. of New South Wales*, 1912, xlvi., 187.

substance, shown by its varying melting-points under different conditions, has made its study somewhat interesting, and, so far as the material at disposal would allow, considerable work has been done with it.

The following data will show how great were the differences between the melting-points of the crystals and those of the same substance after melting :—

(*a*) When the crystals were prepared by crystallisation from alcohol, or from boiling water, they were quite anhydrous, and melted at 122° C., to a transparent resin-like body, without alteration in weight. This fused material was, at first, strongly electric, and had the power of attracting light particles of filter-paper, &c., very energetically. The melting-point of this glassy substance had, by fusion, been reduced to 62—63° C., and so long as it remained in the glassy condition in the lump, the melting-point did not rise, even after many weeks, but if the fused substance was powdered the melting-point commenced to rise at once, and after a comparatively short time this had reached about 120—121°, but did not appear to revert quite to the melting-point of the original crystals.

(*b*) When the fused substance was powdered and the melting-point taken at once, this powder melted at the same low temperature as the spangles of solid material, but if the temperature was continually raised, when this had reached to about 100°, the melted substance became somewhat opaque, but reverted again to the transparent condition at the melting-point of the original substance.

(*c*) When the original crystals were boiled in water they softened and apparently fused at that temperature, and, when the solution had become saturated, remained as fused globules or masses in the boiling water, but soon solidified into a semi-crystalline condition when the water had sufficiently cooled, showing that complete fusion had not taken place, because when fused by dry heat the mass always remained as a glass, and there was no sign of crystallisation during the many weeks it remained under observation. If, however, this glass was dissolved in alcohol it again readily crystallised from this solvent, and the crystals were also readily formed from water when the glassy form was boiled directly in the usual way. When thus re-crystallised, the melting-point of the crystals, both from the alcohol and from the water, had reverted to that of the original crystals, although the melting-point of the fused material from which they had been derived had only been 62—63°.

(*d*) If the melted glassy substance was broken up into small spangles, but not powdered, these became, after several weeks, opaque and yellowish in colour. The melting-point of these opaque spangles had then considerably increased, showing that the tendency is to revert to the higher melting-point in all cases, which may thus be considered the stable condition. How many weeks or months it would take for the melted unbroken glassy lump to revert to the higher melting-point is not yet known, as sufficient time had not elapsed. So far, this has been found to be 62—63°, and in one case three months had passed between the fusion of the substance and the determination of the melting-point. The method of observing the melting-point of the spangles was to place them on a thin glass microscope slide cover-glass, to float this on mercury, and to observe the melting of the spangles with the aid of a lens. At near the melting-point the temperature was only allowed to rise very slowly.

The ready discoloration when bromine water was added to the saturated aqueous solution, with the formation of an insoluble bromide, indicated unsaturation, but this was not confirmed by an alkaline solution of potassium permanganate, as the colour of very dilute solutions remained apparently unchanged for a considerable time, although eventually oxidation to dimethylprotocatechuic acid took place. There appeared to be no alteration on an attempted reduction of the substance, when it was boiled with zinc in an acetic acid solution. The formation of the bromide was also found to have been by substitution, because when bromine was added to a solution of the crystals in carbon tetrachloride, hydrobromic acid was evolved in quantity. Only one atom of bromine was introduced into the molecule by this method, and this was in the side-chain, as the bromine was readily removed by boiling alcoholic silver nitrate. The bromide was practically an amorphous body, and attempts to crystallise it were not successful, nor did it show a well-defined melting-point.

One hydroxyl group was present in the side-chain, but no aldehydic group was formed even with mild reagents, the oxidation to a carboxyl group being direct. The action of concentrated halogen acids also indicated the presence of an alcoholic OH group, and bromine was introduced into the molecule when the substance was boiled in hydrobromic acid. The molecule contains two methoxy groups, and the acid formed by oxidation was veratric acid.

Neither an aldehyde nor carbonyl group was detected, nor were indications for the presence of an ester or of a glucoside obtained.

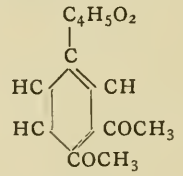
When fused with potash below 200° C., phenolic bodies were principally formed, but when the temperature was increased to about 225° the action became more energetic and the principal product was protocatechuic acid, a very small amount of a volatile acid being produced at the same time. The substance thus has a catechol nucleus.

When more material shall be obtained attempts will be made to determine accurately the arrangement of the atoms in the side-chain. The constitution of the remainder or the molecule is shown from the results.

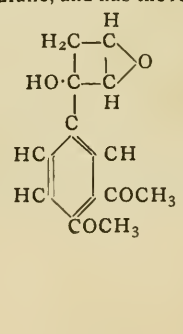
The oxidation to veratric acid, the formation of protocatechuic acid on fusion with potash, the presence of one or more asymmetric carbon atoms, together with the other reactions, suggest a structural formula for this substance in agreement with that of several bodies found in plants, all related to a dihydric phenol, the OH groups of which are in the 3 and 4 positions.

The evidence so far obtained indicates that the crystalline substance which deposits in the timber of *Gmelina Leichhardtii* is new to science, and the name Gmelinol is proposed for it.

The molecule of gmelinol is $C_{12}H_{14}O_4$ and the formula may be arranged as follows :—



The exact positions of the atoms in the side-chain have not been accurately determined, as they can be arranged, theoretically, in several ways. The one perhaps the most promising from general reactions, particularly the red and green colorations given by the vapour to pine-wood moistened with hydrochloric acid, is to consider the side-chain as consisting of furfurane. This is attached to the nucleus by the β' carbon atom, the double bond broken, the valency completed by one hydrogen attached to one β-carbon atom, and a hydroxyl group to the other. The alternative structure for furfurane with only one double linkage answers to requirements better than the usually accepted form. If this arrangement is eventually found to be the correct one, then gmelinol is dimethyoxphenyl-$\beta\beta'$-hydro-oxyfurfurane, and has the following structure :—



The positions of the nitro groups in the dinitro compound are evident.

The characteristic features of gmelinol may, for convenience, be summarised as follows :—Melting-point of crystals, 122° C. (cor.); of fused substance, 62—63°. Needle prisms or plates from hot water. Moderately soluble in boiling water, but little soluble in cold water. Almost insoluble in ether and in benzene. Insoluble in alkalis. Soluble in nitric acid with yellow colour and formation of a dinitro compound. Soluble in concentrated sulphuric acid with a deep red colour. Forms a dark brown amorphous substance when heated with hydrochloric acid. Specific rotation in chloroform $[\alpha]_D = +123{\cdot}3°$. Chromic acid in acetic acid produces dimethylprotocatechuic acid (veratric acid); alkaline solution of potassium permanganate also produces veratric acid. Potash fusion at about 225° gives protocatechuic acid.

Experimental.

In one of the pieces of timber from northern New South Wales a small hollow in the wood had become filled with a solid crystalline mass, the greatest thickness of which was about one-eighth of an inch, but the usual mode of occurrence appears to be in thin veins more or less distinctly crystallised in rosettes. The substance was scraped off and boiled directly in water, filtered boiling hot, the stem of the funnel being lightly plugged with cotton-wool. As the water cooled, well-defined crystals formed, which, when of sufficient size, fell to the bottom of the vessel. This procedure was repeated three or four times, by which time the crystals had become colourless and appeared to be pure. The usual method of preparation was to saw the unsound timber into small pieces, divide along the "shakes," and trim the sides with a chisel. The shavings so obtained were then heated in alcohol to dissolve the substance, filtering the alcohol through cloth. Although it is somewhat soluble in hot alcohol, yet, if this was deficient in amount, a quantity of the substance soon separated on cooling. This separated portion was, however, identical in composition with that remaining in solution, as its identity was determined by separate purification. The alcohol was partly distilled off, and the remainder evaporated down to a small bulk which formed a crystalline mass on cooling. These impure crystals were then dissolved in boiling water, a portion at a time, filtering boiling hot, and this process repeated until the crystals were pure.

The crystals as thus obtained from water were rhombic prisms or plates, and they polarised very well in colours. They were of a glistening nature, and had altogether a brilliant appearance.

The crystals were insoluble in petroleum ether, slightly soluble in ether and in benzene, somewhat soluble in hot alcohol, but not very soluble in cold alcohol. They were exceedingly soluble in chloroform and carbon tetra chloride, but from these solvents a varnish remained at first, which slowly reverted to the crystalline form after several days.

The crystals dissolved in boiling water, but not very readily, separating out again on cooling. The pure crystals required 1470 parts of cold water at 22° C. to dissolve one part of substance, and the purest crude material in the wood was only soluble 1 part in 1315 parts of cold water at the same temperature, indicating the comparative absence of soluble impurities associated with the crystalline deposit when in the wood.

The aqueous solution of the pure crystals was quite neutral, and did not reduce Fehling's solution, either before or after boiling in acid. An ammoniacal solution of nitrate of silver was slightly reduced on long boiling. No coloration was obtained with ferric chloride, and the usual reagents gave no precipitate, except a very slight one with basic acetate of lead. The crystals were insoluble in potash and in the alkalis generally, even on boiling, except when the solution was sufficiently dilute to act like water, in which case the crystals separated unchanged on cooling.

In glacial acetic acid the crystals dissolved readily and without colour. With nitric acid they dissolved with a yellow colour forming a dinitro compound. With sulphuric acid they dissolved forming a very deep ruby or reddish brown colour, and on adding water a purple-brown precipitate separated. When heated with hydrochloric acid a dark brown amorphous substance was produced.

Analyses of the crystals gave the following results :—

0·1872 grm. gave 0·4444 grm. CO_2 and 0·1066 grm. H_2O; C = 64·74 and H = 6·327 per cent.

0·1574 grm. gave 0·3740 grm. CO_2 and 0·093 grm. H_2O; C = 64·803 and H = 6·565 per cent.

$C_{12}H_{14}O_4$ contains C = 64·865 and H = 6·307 per cent

The molecular weight was taken in Beckmann's apparatus using alcohol as the solvent.

0·4775 grm. in 16·4 grms. alcohol increased the boiling-point, 0·16°. The molecular weight calculated from this is 209. By the freezing method with acetic acid as solvent, one determination gave 228 as molecular weight, but with other trials abnormal figures were obtained; this was also the case when boiling chloroform was used as solvent.

From the results in other directions it is necessary that four atoms of oxygen at least should be present in the molecule, so that $C_{12}H_{14}O_4$ may be assumed to be correct.

Optical Rotation. The optical rotation was taken in chloroform as this appeared to be the best solvent for the purpose.

0·3 grm. crystals in 10 cc. $CHCl_3$ rotated the ray 3·7° to the right in 100 mm. tube; the specific rotation from this $[\alpha]_D = +123{\cdot}33°$.

0·6 grm. crystals in 10 cc. $CHCl_3$ gave rotation 7·4° to the right in the same tube, showing the specific rotation to be the same for both.

0·3 grm. crystals was just melted in a beaker, the glassy substance dissolved in chloroform and made up to 10 cc., the optical rotation was again +3·7°, so that no alteration was observed between the crystalline and amorphous conditions of the substance.

The molecule thus contains one or more asymmetric carbon atoms, which, from the known constitution of the remainder of the molecule, must be in the side-chain.

Dinitro Compound.—The crystals were dissolved in nitric acid, and gently heated to start the reaction. When this was completed the addition of water gave a lemon-yellow precipitate, which, when purified, was soluble in, and crystallised from, both ether and alcohol. It was readily purified from boiling water in which it readily dissolved, but separated out again in masses of yellow felted crystals on cooling. The melting-point was sharp at 128—129°, although it agglutinated some degrees below that temperature.

0·1756 of the nitro compound gave 14 cc. of nitrogen at 17° C. and 755 mm. pressure, which equals 9·14 per cent nitrogen. $C_{12}H_{12}(NO_2)_2O_4$ contains 8·98 per cent nitrogen. It is thus shown to be a dinitro compound.

Methoxy Groups.—The ready formation of insoluble halogen compounds when the crystals were boiled in a halogen acid made the results somewhat erratic. Figures more nearly correct were obtained when acetic anhydride was added, but even then the results were not too satisfactory. The greatest amount of silver iodide obtained in six determinations only represented about one and three-quarter groups of OCH_3, but this, together with the formation of veratric acid on oxidation, is sufficient confirmation for two OCH_3 groups in the molecule.

Hydroxyl Group.—A portion of the crystals was boiled with acetic anhydride and sodium acetate in the usual way. On the addition of water a crystalline substance separated, which, when purified from acetic acid melted at 110° C. Analysis gave results in conformity with one OH group. When saponified by boiling with standardised alcoholic potash the following results were obtained :—0·3684 grm.

boiled two hours had used 0·0756 grm. KOH. 0·41 grm. boiled one hour had used 0·084 grm. KOH. $C_{12}H_{13}(OCCH_3)O_4$ would require 0·0781 grm. KOH in the first instance, and 0·087 grm. KOH in the second. One hydroxyl group is thus indicated, and as this is not phenolic it must be in the side-chain.

Bromide.—The bromide was formed by the addition of bromine water in excess to the saturated aqueous solution of the pure crystals. It was light drab in colour, and was not distinctly crystalline. When well washed and purified from ether it melted at about 100°, darkening much at about 90°, but the melting-point was not sharp.

Determination of the bromine gave the following results: —0·3435 grm. gave 0·2114 grm. AgBr = 26·2 per cent bromine. 0·1554 grm. gave 0·0985 AgBr = 26·9 per cent bromine. $C_{12}H_{13}BrO_4$ contains 26·58 per cent bromine. One bromine atom had thus been introduced into the molecule. When the bromide was boiled in alcoholic silver nitrate, a precipitate quickly formed; the metallic silver was boiled out from this with dilute nitric acid, the residue washed, dissolved in ammonia, and precipitated again by nitric acid. The bromine atom was thus shown to have been introduced into the side-chain.

Oxidation.—The crystals were dissolved in glacial acetic acid and chromic acid in the same solvent slowly added until in excess. The oxidation commenced at once with the evolution of heat, the flask was then cooled under the tap. A chromium salt, which appeared to be insoluble in glacial acetic acid, continued to form until the reaction was complete. This salt was filtered off through cloth, squeezed, and the solid cake thus obtained dissolved in water, in which it was readily soluble. The solution was then acidified, extracted with ether, and after the removal of the acetic acid a solid acid remained. This was dissolved in dilute alkali, filtered, acidified, and the solution extracted with ether. The acid thus obtained was fairly soluble in boiling water but precipitated again on cooling, so that it could be easily purified. The acid sublimed unchanged. The melting point of the sublimed acid was the same as that of the acid obtained from water; this was 180° C. (cor.). It was found to melt at identically the same temperature as a sample of pure veratric acid, nor was the melting point different when equal parts of the new acid and veratric acid were mixed together. The molecular value was determined by titration and agreed very well with that of veratric acid.

When a very dilute alkaline solution of potassium permanganate was added to a large quantity of a saturated aqueous solution of the crystals the colour remained persistent for a long time; it then slowly faded with the formation of the oxide of manganese; oxidation had thus taken place. The acid formed in this way was collected, purified by sublimation, and found to melt at the same temperature and to be identical with the acid formed by oxidation with chromic acid. It was thus veratric acid.

It is apparent that oxidation of the side-chain had taken place in both instances, with the formation of dimethyl-protocatechuic acid.

When oxidised with bichromate of potassium and sulphuric acid with the aid of heat, the action was too energetic, and most of the substance was destroyed by this method.

Potash Fusion.—When the crystals were heated with potash at a temperature not exceeding 200° C. for one-half hour, the colour of the melted substance had become very dark, and phenolic bodies were largely formed. The odour of creosote was most marked. The melt was dissolved in water, and the solution repeatedly agitated with ether to remove the unaltered substance. The remainder was acidified, extracted with ether, and the ether evaporated. The residue was treated with a solution of sodium carbonate, to fixed the small amount of acid formed at the same time, and this solution again extracted with ether. The phenol thus obtained had a marked creosote odour, was but little coloured, was semi-solid, and practically insoluble in water. The alcoholic solution was coloured a bluish green to dark green with ferric chloride, indicating its relation to the catechol group.

A fresh portion of material was fused with potash between 210° and 225° C. for one hour. The action was more energetic at this temperature, with frothing and evolution of hydrogen. The melt was dissolved in water, when the creosote odour was again observed. The solution was acidified, and three-fourths distilled over, and although acid, yet the amount of free acid formed was very small indeed. The remainder was agitated with ether, the ether evaporated to dryness, the crystalline residue dissolved in sodium carbonate, and agitated with ether to remove the small amount of phenol. The alkaline solution was acidified, extracted with ether, the ether evaporated, the residue dissolved in water, and decolorised by boiling with animal charcoal. The crystals finally obtained were very soluble in water, melted at 198°, and gave all the reactions for protocatechuic acid. The yield of acid formed in this way was very good.

In am indebted to my colleague, Mr. R. T. Baker, F.L.S., the Curator, for botanical information, and to Mr. Roughley for photographs.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Fleas can Transmit Infectious Diseases.

The flea has already been the object not only of male. dictions but also of serious allegations. Like many other insects, it is not content with victimising human beings, but it must also inoculate them with infectious germs. In a note presented to the Academy of Sciences of Paris, M. Laveran has indicated that all kinds of fleas do not offer the same dangers. The eminent hygienist has, however, signalled most particularly the flagellant flea, which secretes in its intestine a very dangerous parasite. The flagellants also are sometimes to be met with in the dog. It results, from certain experiments made at the Pasteur Institute, by MM. Laveran and Francini, that mice have been infected by injecting into their peritoneum the contents of these parasites diluted in a little physiological water. This had already been remarked in 1912 by Lafont, who had operated with a flagellum from the digestive tube of a bug. M. Laveran has not stated whether men or dogs could be infected by the contact of these fleas, but the effect produced upon the mouse is sufficient to make us uneasy. So let us continue to fight against this troublesome insect and to destroy it everywhere by all the means in our power.

The Consumption of Paper.

Paper may be divided into three great classes—fine, high-class, ordinary paper for current uses, and paper for folding. It is certain that the consumption of the higher classes of paper is increasing, but very slowly, and this industry will always find sufficient raw material for its requirements, more especially as the scale of its prices is very elastic. The same cannot be said for the second class, that of paper for ordinary use; that is to say, paper intended for daily uses, such as newspaper editions, prospectuses, and generally speaking for all printed and written matter. It is this consumption that is continually increasing, and whose needs and demands of paper are ever becoming more and more imperious. It is in order to fulfil these requirements, considerably increased by the use of rotary printing machines, with a large output, that the stationery industry has also been obliged to create paper machines of great width and great speed, which can turn out as much as forty or fifty tons of paper in twenty-four hours; it is also for this kind of paper the forests are pillaged. When there is no longer a sufficient quantity of wood to be had, with what will these paper-mills be fed? At that moment the only wood remaining

will be that obtainable from the annual growth of forests reserved and arranged for periodical cuttings, and the stationery industry will have to share them with other industries. M. Henry Montessus de Ballore, in his interesting technical work, tries to solve the question concerning the future resources in raw material of paper manufacture. He has drawn up a list of those materials of which the cellulose could be used for the manufacture of paper.

Besides wood, to feed the paper-mills in the future, we have: Plants that grow spontaneously, bamboo, papyrus, alfa; the refuse of various industries, rags, cables, cords, strings; the refuse of spinning-mills, cotton, linen, hemp, jute, phormium; the refuse of agriculture, wheat and rye straw, oat and rice straw, the stalks of Indian-corn, and the refuse of the sugar-cane.

M. de Montessus de Ballore has specially studied each of these matters, their treatment, their yield, and the rise of the pastes obtained; lastly, he has noted some plants that, at least for the present, appear to have only a very restricted future in the paper industry.

Variability of Nebulæ.

The question of the variability of the brillancy is now discussed after having been considered as certain. Astronomers are to-day apt to look upon it as doubtful, and that on account of the difficulty of conceiving the mechanism of such a variation, as much in the case of resolvable nebulæ or masses of stars as in the case of non-resolvable or purely gaseous neublæ. A nebula discovered by Hind in 1845, in the constellation of the Eagle, was considered as variable; quite recently, M. Borelly announced that at present it appears to be attaining a maximum state of brilliancy. M. Bigourdan shows that former observations do not confirm the variability. He insists on the interest of the fact noticed by M. Borelly, and on the importance just at present of the observation of the Hind Nebula, as this is just now very distinctly visible in instruments of average opening.

The Aerial Gulf Stream.

The Gulf Stream, when it leaves the Gulf of Mexico, enters the Atlantic with a speed of 8 kilometres an hour. It is 60 kilometres wide and 400 metres deep, and daily transports about 40 millions of milliards of calories. This enormous quantity of heat, of which it is almost impossible to obtain an exact idea, plays a fundamental rôle in the general climatology of the earth. Strangely enough it is this stream of hot water, exercising its temperate action on the coasts it waters, which is the direct cause of the existence of deserts. And this is how. Water is one of the bodies in which heat is the most easily preserved, and consequently the Gulf Stream even in high latitudes still keeps an enormous quantity of heat. The masses of air that rest on these hot waters are kept at a temperature higher than the surrounding temperature and form a veritable aërial gulf stream superposed over the marine current. But the aërial current is not like the marine one arrested by the mass of the continents. It continues its route above Europe, abandoning, in the form of rain, the enormous masses of water it contains; it is these abundant precipitations which feed the numerous lakes of Sweden, Finland, and Northern Russia. But, on account of the rotation of the earth, the aërial current turns first to the east, then inclines towards the south. It thus constitutes masses of dry cold air which give to the plains of Russia their principal meteorological character. As it draws nearer to the Equator the current is again warmed, but remains at the same time dry and without vapour; its direction is then north-east, and it is in the state of a drying wind that it blows over the regions it crosses. It is the origin of the band of deserts of Turkestan, Arabia, Sahara, which are to be found on its return route. After having left the Continent, the aërial current, thanks to the trade-winds, links itself on again to its starting point, the Gulf Stream, thus looping its circuit after having, like everything else, done much good and much evil.

Electromagnetic Waves.

The laws governing the propagation of radio-telegraphic signals in the atmosphere during the day and during the night are still but imperfectly known, and the development of aëronautics has enabled us to gather some interesting information on this subject. The signals grow weaker as the distance increases, but one of the points to be examined is to know how the height above the ground influences this problem; in other words, are the signals affected by a weaker density, a lower temperature, and by the intense ionisation of the high regions of the atmosphere. M. G. Lutz has given several results obtained in utilising a balloon of 1680 cubic metres, with a circumference of 45 metres. The autenna was formed by a metallic wire of 100 metres long hanging under the basket. During the experiments made in the night, the balloon covered a distance of 120 kilometres at an average altitude of 1277 metres. It was found that the intensity of the signals received decreased when the distance increased, but that this weakening is not proportional to the square of the distance; it varies as the power 1·96 of the distance and when far from the starting station, as the power 0·88. At an equal distance it is remarked also that the signal is so much the weaker as the balloon is higher. To be more precise on this point, a second ascension was made, the balloon then rising to a height of 6500 metres. At this height, the intensity of the signals equalled what they would have had on the earth at the same distance from the station. These results are worth being confirmed and completed, for the question is still but very incompletely known, and up till now the experiments have been insufficient.

NOTICES OF BOOKS.

Studies in Valency. By F. H. Loring. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

In this little book certain relations between the combining powers of the elements are shortly discussed, and some new lines of experimental work are suggested. The valencies of some of the elements which are specially interesting, such as vanadium and bismuth, are treated in detail, and a chapter is devoted to the consideration of electricity as a conditioning agent in chemical changes, and another to modern theories of atomic structure based upon experiments in molecular physics. The author has evidently carefully studied the literature of theories of valency, and he shows much skill in stating briefly the gist of an argument and ingenuity in pointing out the directions in which fruitful research may possibly be undertaken.

Laboratory Methods in Agricultural Bacteriology. By F. Löhnis, Ph.D. Translated by William Stevenson, B.Sc., N.D.A., N.D.D., and J. Hunter Smith, B.Sc., N.D.A., N.D.D. London: Charles Griffin and Co., Ltd. 1913.

The need of such a work as this in the English language has long been felt by agricultural teachers and students, who have found considerable difficulty in devising and satisfactorily carrying out the practical work in bacteriology which is an essential complement of the study of the theory of the subject. The technique of bacteriology is first described, and clear directions are given for preparing culture media and isolating and examining bacteria. The use of only comparatively simple apparatus is recommended, and sources of error to be avoided, and the precaution which must be adopted to ensure successful work are repeated pointed out and emphasised. The application of general methods to dairy, manure, and soil bacteriology is then described in detail. Tables are given for the identification of bacteria, and the question of laboratory equipment is shortly discussed. The book is sure to

receive a hearty welcome from the many agriculturists who, while unable to study bacteriology in Prof. Löhnis's own laboratory at Leipzig, are fully aware of the importance of the subject as applied to agricultural problems and of the great value of his work in it.

Simplex Atomic Models. Designed by E. G. LESTER, B.Sc. Birmingham: Philip Harris and Co., Ltd.

TEACHERS of chemistry will undoubtedly find that these models greatly diminish the difficulties of theoretical chemistry for the young beginner. They have the advantages of being simple and cheap, and by means of them the boys can themselves build up structural formulæ, work out equations, and illustrate the laws of chemical combination, while they should be simultaneously acquiring clear ideas of valencies, variable valencies, &c. The boxes of models contain a little stand, a number of wire links, and detachable cardboard discs (pink in the case of non-metals, white for metals) with the symbol, valency, and atomic weight of the elements printed on them. Some blank discs are also included for use as compound radicles. With the necessary links and discs the pupil can build up such formulæ as $\begin{matrix}Na—O\\Na—O\end{matrix}\!\!>\!S\!\!<\!\!\begin{matrix}=O\\=O\end{matrix}$, &c., and it will undoubtedly mean much more to him than the same formula written on a blackboard. It may of course be objected that he will form some very concrete and erroneous conceptions as to valencies, but that is perhaps unavoidable, at any rate in an elementary exposition of the subject, and in the hands of a good teacher the models should be a valuable educational aid. By bending the wire links the models can be used to illustrate the arrangement in space of carbon compounds.

Metropolitan Water Board. Ninth Research Report. By Dr. A. C. HOUSTON.

THE ninth research report of the Metropolitan Water Board contains accounts, with tables and diagrams, of the search for pathogenic microbes in raw river water and for the typhoid bacillus in sewage. The results of the investigations show that the purification processes practised by the Board amply safeguard the health of the metropolis. The consideration of the question, "Where is the typhoid bacillus?" appears to lead to the conclusion that its home is not so much in impure water, nor even in crude sewage, as in the "factories" of disease, as exemplified by the "carrier" case.

OBITUARY.

DR. LOUIS MERCK.

DR. LOUIS MERCK, the head of the famous firm of E. Merck, of Darmstadt, died on September 15th after a short illness. He had been connected with the firm for over thirty years, and for twenty-five years had been its senior partner. The growth and wonderful success of the house were largely due to his foresight, energy, and enterprise, and his loss will be very severely felt.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 13, 1913.

Cryoscopy in Fused Hydrated Salts.—Ch. Lenhardt and A. Boutaric.—The melting-point of a hydrated salt is lowered by the presence of a dissolved substance, and it is the same with the equilibrium temperature which is established between two solid hydrates and an excess of solution. The authors have investigated whether the cryoscopic formula of van't Hoff, $K = 0{\cdot}01985\ T^2/L$, is applicable to these phenomena, and, using sodium hyposulphite with five molecules of water and sodium sulphate with $10H_2O$, they have found that the formula holds good.

New Physico-chemical Volumetric Method.—René Dubrisay.—The author has devised an acidimetric method, based upon capilliary phenomena, which is both simple and accurate. He makes use of the fact that when an oil is shaken with water containing alkali, the drops formed remain in suspension and an emulsion is obtained. When the water is neutral or acid no emulsion is formed, but after a few moments the liquid divides into two layers. According to Tate's law, the weight of a drop of liquid which detaches itself from the extremity of a pipette is proportional to the superficial tension of the liquid. Thus if N is the number of drops corresponding to the flow of an invariable volume $N = A/\delta$, where δ is the superficial tension and A is a constant. If the drops are counted when oil of vaseline flows into a solution of acid to which increasing quantities of alkali are added, and the results are expressed graphically, it will be seen that the curve has an abrupt turning point at the point of neutralisation.

Catalytic Preparation of Ketones.—A. Mailhe,—The author has repeated his experiments on the catalytic preparation of ketones, using zinc or cadmium oxides as catalysts, since his results were questioned by M. Senderens. He finds that both oxides, either alone or mixed with the metals, are good catalysts, except in the case of isobutyric and isovaleric acids, which give either very poor yields of ketone or none at all. Calcium carbonate is also a good catalyst for acids.

Nitro Derivatives of *p*-Phenetidine.—Frédéric Reverdin and Ludwik Fürstenberg.—Of the nine possible nitro derivatives of *p*-phenetidine three only have hitherto been described. By the nitration of the acyl derivatives of the base the authors have now succeeded in preparing three new compounds, viz., the 3.5-dinitro derivative, the 2.6-dinitro derivative, and the 2.3.5-trinitro derivative.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 10, 1913.

Compounds of Monovalent Nickel.—J. Bellucci and R. Corelli.—Red solutions of nickel cyanide evolve hydrogen at the ordinary temperature, and measurements of the amount evolved show that it corresponds with that which would be generated in the change from NiX to NiX_2. Iodometric determinations also show that the red solution also contains a compound of monovalent nickel.

Action of Hydroxylamine on Ketones of the Type R.CH:CH.CH:CH.COR.—R. Ciusa and G. B. Bernardis.—When hydroxylamine hydrochloride acts on the ethyl ether of cinnamilidenepyruvic acid a substance of formula $C_{26}H_{34}O_9N_4$, fusing at 213°, is obtained. It contains a molecule of alcohol of crystallisation, and is formed by the union of two molecules of the hydroxylamine oxime of cinnamilidenepyruvic acid, combined in such a way as to mutually saturate the double bonds. The substance $C_{24}H_{28}O_8N_4.C_2H_5OH$ immediately gives an insoluble sodium salt when treated with sodium carbonate. It is decomposed by boiling with dilute sulphuric acid. In the original reaction a small amount of a substance of formula $C_{26}H_{31}O_8N_4NO$ is also obtained.

NOTES AND QUERIES.

Aluminium Sulphate.—A correspondent asks for a reference to a process for manufacturing aluminium sulphate from bauxite by the use of gypsum instead of sulphuric acid.

MEETINGS FOR THE WEEK.

FRIDAY, 10th.—Biochemical Society, 8.30. (In the Department of Chemical Pathology, St. Thomas's Hospital, London).

— Alchemical Society, 8.15. (At International Club, Regent Street). Address by the Hon. President, Prof. John Ferguson, M.A., LL.D., &c.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2811.

THE CHEMISTRY OF THE RADIO-ELEMENTS.*

By ALEXANDER FLECK, B.Sc.,
Assistant in the Department of Physical Chemistry, Glasgow University.

The fact that it is impossible to separate some of the radio-elements from some one or other common element is not a new one. Welsbach has attempted to separate thorium and ionium, Herschfinkel and Hevesy and Paneth have tried radio-lead (radium D) and lead, Hahn and Boltwood radio-thorium and thorium, Hahn thorium X and mesothorium-1, Marckwald and Soddy mesothorium-1 and radium, and Marckwald and Keetman uranium X and thorium, but in none of these cases has it been found possible to separate one element from the other once the two had been mixed together in solution. It was to be expected, therefore, that similar cases would exist among the shorter-lived radio-elements, and it is proposed to describe briefly the experimental methods that have been employed in examining the chemical nature of these substances.

In the first place it has to be noticed that, as a rule, we have to find the chemical nature of unweighable quantities of material. To give two examples, the amount of uranium X in equilibrium with 50 grms. of uranyl nitrate is as much as can be conveniently worked with, and this quantity weighs only 10^{-9} of a grm. In the case of radium A this quantity is far too large and 10^{-12} grm. is ample for most purposes. It is therefore evident that the chemical nature of these bodies must be worked out in the presence of what is really an impurity of many thousand times the actual weight of the radio-element present.

The first step in the determination of the chemical nature consists in finding what known element our radio-element most resembles. This is done by making a mixture of three elements in solution—two ordinary elements which can be easily isolated and the radio-element. The two elements are then separated and each portion tested under the electroscope, when it will usually be found that the radio-element is definitely associated with one or other portion. For instance, if we have a solution of thorium B, iron, and calcium, and ammonia is added to the solution the thorium B will be found to be precipitated with the iron. By a number of such experiments it can be shown that thorium B must belong to the first, second, or third group of metals, and by a similar process, say, with a mixture of copper and iron, the third group is eliminated and it must belong to the first or second. Sometimes it happens that the radio-element does not identify itself solely with either of the common elements, as when we separate a mixture of iron and uranium containing mesothorium-2, but divides itself between the two, but as a rule by proceeding in the manner indicated it is possible to say that the radio-element resembles in a general way one of the common elements, as, for example, radium E and bismuth. The second step is to find whether this resemblance amounts to an identity or is merely a similarity, as polonium and bismuth. It is well known that if a mixture of polonium and bismuth is heated strongly the first fractions to volatilise are richer in polonium. The method then consists in making a mixture of the radio-element and the common element, to which the former bears most resemblance, and submitting the mixture to some fractional treatment, the exact nature of which is, of course, dictated by the nature of the common element. In the case of thorium B, which was known to resemble lead, a quantity of lead chloride which had been crystallised from a solution containing thorium B was volatilised in a vacuum, and thus divided into fractions in the order of their volatilities. Successive measurements of the activity of these fractions were taken over a period of twenty-four hours, and thus the relative quantities of thorium B in each one obtained. The quantity of lead in each was then estimated by the usual gravimetric process, and in this way the activity per grm. of lead in each fraction was obtained, and it was found that for any one experiment this quantity was constant within the limits of experimental error. In all such cases β-rays were used to determine the quantity of the radio-element present, and the common element was there in such small quantities, usually spread out in a thin layer, that the absorption of the β-rays by it was negligible. By such methods the following results were proved:—

1. Uranium X and radio-actinium are chemically identical with thorium.
2. Radium C, thorium C, actinium C, and radium E are chemically identical with bismuth.
3. Radium B, thorium B, and actinium B are chemically identical with lead.
4. Thorium D and actinium D are chemically identical with thallium.

Mesothorium-2 was the first case that was met with in which it was impossible to find a resemblance to a common element, and when its analogy with actinium was suspected special methods had to be devised for the measurement of the latter element, since it itself is rayless and since it has not been possible to obtain it free from other matter. Mesothorium-2 was separated from a strong mesothorium preparation in solution by the precipitation of zirconium hydroxide, and this small quantity of material added to an acid solution of actinium contained in lanthanum. The actinium had been freed a very short time previously from radioactinium and actinium X, and was therefore rayless. The solution thus obtained contained mesothorium 2, actinium, zirconium, and lanthanum, of which only the first gave β-rays. The solution was then fractionated, and during the two following days β-rays were measured, and thus a measure of the quantity of mesothorium-2 in each fraction was obtained. In the course of two to three months the actinium had grown radioactinium and actinium X, which in turn had grown actinium D, a β-ray-giving body, and the measure of the activity then was a measure of the amount of actinium present. In this way it was found that the ratio of mesothorium-2 to actinium was constant.

The second case when no resemblance with a common element was found was radium A and polonium. In this case to measure radium A and polonium when both were present, use was made of the difference of the ranges of the α-particles coming from these substances. To obtain quantitative information regarding the identity of the two, the only way that was found possible was to deposit both simultaneously on gold, platinum, silver, or copper plates. In every experiment it was found that the ratio of polonium on any two plates was approximately equal to the ratio of radium A. Absolutely exact experiments were not possible, since the radium active deposit had to be dissolved from a magnesium plate, the solution thus obtained added to the polonium solution, the deposit obtained on the plates, which had then to be washed and dried, and sufficient readings for each plate had to be taken, all within seven or eight minutes from the instant of the withdrawal of the active deposit from the emanation.

The last part of the work concerns the chemical nature of uranium X_2, which has recently been discovered by Fajans and Göhring, and which has a period of half value of 1·1 minutes. This body is not precipitated as sulphate, but otherwise is very easily precipitated, and this is in complete agreement with what one might predict from its position in the V. A family of the Periodic Table. It

* A contribution to the discussion on "The Radio-elements and the Periodic Law," in Section B, British Association, Birmingham, 1913.

would be expected also that this substance should be volatile in the presence of hydrofluoric acid, since tantalum fluoride—a volatile body—is more volatile than the corresponding salt of niobium. However, it was found to be absolutely non-volatile, but it must be remembered, to repeat an observation made in *Nature* some time ago in a different connection, that whereas Mendeleeff made his predictions by interpolation. in this case it was necessary to extrapolate, and thus some uncertainty is introduced. The general similarity of Uranium X_2 to tantalum is shown by Hahn and Meitner's experiment, that if a solution of uranium X is filtered through a layer of tantalum pentoxide, the uranium X_2 alone is adsorbed.

One point that may be referred to is the relation between the radio-elements and the rare earths. The question may be asked: Is it not possible that the so-called non-separable elements, *e.g*, thorium, radiothorium, ionium, uranium X, and radioactinium, stand to one another in the relation of a rare earth group, and if that was so could we detect the fact? The electroscope gives us a means of detecting minute variations in the concentration of the radio-element, and when no alteration in concentration was found, after ten successive precipitations within a limit of experimental error of about 4 per cent, the experimental evidence shows that these radio-elements are not analogous to the rare earths. By rearranging the Periodic Table, as has been done by Werner, it has been possible to find a place for all the rare elements, but in no system that has been put forward yet would it be possible to get the thirty-eight radio-elements into the last series. No provision is made in the ordinary Periodic Table for bodies having the same atomic weight but different properties, such as we have in the radio-elements, *e.g.*, mesothorium-2 and radiothorium. These bodies have the same atomic weight, but can be separated from one another as easily as iron from calcium. Finally, our chief evidence for the existence of a number of rare earths is differences in their spectra, while the spectra of non-separable radio-elements are believed to be identical, although it must be remembered that there is only the one case of thorium and ionium where this has been proved. These considerations show that we are not dealing with substances similar to rare earths, and that there is no analogy between the two cases.

It is to be noticed that in all cases in which the non-separable elements are common elements these latter all have atomic weights of over 200, and occupy one or other of the last twelve places in the Periodic Table.

In conclusion, in addition to the results already given, we have the following, obtained by special methods:—

5. Mesothorium-2 is chemically identical with actinium.
6. Radium A is chemically identical with polonium.
7. Uranium X_2 has a chemical nature peculiar to itself.

Although these results are often put in an apparently negative form—that thorium B is non-separable from lead, &c.—this is not a negative statement, but is merely a convenient way of stating that these radio-elements have characteristic chemical properties and can be separated from any of the other eighty or so elements.

Physical Chemistry Department,
Glasgow University.

THE ACTION OF AN ALKALINE NATURAL WATER ON LEAD.*

By J. F. LIVERSEEGE and A. W. KNAPP.

THE water supply of Birmingham is gathered chiefly in Wales. The water is slightly alkaline: it does not appreciably *dissolve* lead (absence of "plumbosolvency"), but unless treated it corrodes or "*erodes*" bright sheet lead. To prevent any danger from this action, a small proportion of powdered chalk is added to the water in Wales. This treated water flows to Birmingham through an aqueduct seventy-three miles long.

Lead Pipes.—For these experiments a series of lead pipes was connected with the supply and analyses of the water made over a period of five years. Hundreds of samples were also taken from consumers' pipes and from lengths of lead pipes closed with corks. For short periods the total lead dissolved from the pipes increased with time, but different lengths of the same pipe showed considerable variation. As a rule a pipe becomes with age less sensitive to the action of the water, but the rate of this change varies greatly with different pipes. Treatment of new pipes with a dilute solution of potassium permanganate gave them a considerable power of resistance to the action of the water.

Sheet Lead.—Many experiments were made on the sheet lead "erosion" test, and for practical purposes a duration of one day is preferred to the seven or fourteen days suggested by Dr. Houston. We find that erosion is due to the action of oxygen in the presence of water. The amount of lead eroded is affected by the distance from the lead to the water surface, is generally proportional to the area of the surface of the lead exposed, and does not depend on the volume of the water.

With untreated water carbon dioxide up to one per cent by volume produced little effect on the amount of erosion; when two or more per cent of carbon dioxide is present erosion no longer occurs, for the liquid remains clear, but lead is dissolved, in amount much less than that removed by erosion. Given sufficient oxygen, the alkalinity of the water is the principal factor determining the amount of erosion. The use of (*a*) *lime* to prevent erosion was not found satisfactory, the presence of three to nine parts per 100,000 of water reduced the erosion, but smaller or larger quantities were of little, if any, use. Four parts per 100,000 of (*b*) *calcium carbonate* gave protection, and as little as two parts per 100,000 of (*c*) *calcium bicarbonate* were sufficient to practically prevent erosion. Filtration through sand had little effect on the action of the water on lead. No evidence was found of a seasonal variation in the action of the water on lead, though the colour and amount of organic matter varied considerably.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

DIRECT DETERMINATION OF THE STEATITE OR TALC-FACING ON RICE.

By E. W. T. JONES, F.I.C.

THE following is a simple and expeditious way of doing this, and is independent of any variation in the natural ash of rice:—

Put 5 grms. of the rice into a 150 cc. squat beaker, pour on to it, say, 20 cc. of ether, and agitate for a few minutes; pour this off into an 80 or 100 cc. beaker containing a cc. or so of water, and evaporate the ether off on the top of the water-oven. Allow the ether to evaporate from the rice, then add to it about 15 cc. of cold distilled water, and agitate; pour off into the other beaker, and repeat four or five times till the water comes away almost clear; allow these washings to stand all night, then the nearly clear supernatant liquid can be poured off, leaving the steatite associated with a little fine rice behind; transfer this by means of a wash-bottle (I use methylated spirit to facilitate evaporation) to a weighed platinum dish, evaporate to dryness, ignite, and weigh; this gives the amount of steatite or talc-facing.

The first treatment with ether removes any oil which may tend to retain the facing, and the subsequent water dissolves the glucose fixing the same.

Wolverhampton, September 16, 1913

A NEW METHOD FOR THE DETERMINATION OF THE MOLECULAR WEIGHT OF STARCH.

By CECIL L. HORTON.

The general formula for starch is given as $(C_6H_{10}O_5)_n$, but if we assume the compound to be a chain of dextrose molecules, built up by condensation with the elimination of water, we arrive at the formula $\{(C_6H_{12}O_6)_n-(n-1)(H_2O)\}$ ("Hollemann's Organic Chemistry"). If n is large the difference in the molecular weights obtained is very small; *i.e.*, if $n=41$.

$$(C_6H_{10}O_5)_{41} = 6642,$$
$$\{(C_6H_{12}O_6)_{41}-40(H_2O)\} = 6660,$$

and difference = $\frac{1}{4}$ per cent.

If therefore the hydrolysis starch $\rightarrow$ dextrose can be completely carried out without the production of other substances, 1 molecule of starch will create n molecules of dextrose with the absorption of $(n-1)$ molecules of water. The molecular weight of starch becomes—

$$[(180n)-(n-1)18] = 18(9n+1),$$

that of sugar being 180 and water 18.

If therefore W grms. of starch give rise to W_1 grms. of dextrose, then—

$$W : 18(9n+1) = W_1 : n180.$$
$$\therefore Wn\ 180 = 18W_1(9n+1).$$
$$\therefore n(10W-9W_1) = +W_1.$$
$$\therefore n = \frac{W_1}{10W-9W_1}.$$

Therefore by determining the weight of sugar obtained from a given weight of starch the value of n can be found. The number is of course a whole number, and by substitution in the formula $[M]=18(9n+1)$, the molecular weight can be found.

The writer some months ago endeavoured to obtain the value of n, but was unable to discover a suitable catalyst, the ordinary alkali and acid obtainable causing the formation of a brown humus in sufficient quantity to render the observations worthless. This question is still under consideration.

THE ESTIMATION OF CHLORINE IN RAG FLOCK.

By ALBERT E. PARKES, F.I.C.

The estimation of chlorine in rag flock is now an undertaking which many analysts are called upon to perform, and methods have already been recommended by Richardson and Jaffé (*Journ. Soc. Chem. Ind.*, 1913, p. 402), and Black (*Analyst*, 1913, p. 409).

Since the Rag Flock Act came into force in July, 1912, the writer has examined a large number of samples from various sources, and at the outset devoted some time to devising a suitable process for the chlorine estimation. It was very early found that the gravimetric method applied to the aqueous extract was unreliable owing to the precipitation of other substances with the silver chloride, and the direct volumetric method could only be used when the solution was colourless. As most flocks contain soluble dyes this occurs but seldom. Finally it was found that the best results were obtained by evaporating the aqueous extract to dryness, heating to destroy organic matter, and titrating the chlorine with standard silver nitrate solution.

The complete method now adopted is as follows:—

Fifty grms. of the well-mixed sample is weighed out, placed in a large beaker with about 500 cc. of distilled water, and allowed to digest at laboratory temperature for three to four hours. It is then thrown on to a Buchner funnel in which a circular piece of fine metal gauze has been fitted. By means of the filter-pump the flock is drained, pressed dry by hand, and washed on the funnel with successive quantities of 100 cc. of water, draining and pressing between each washing, until 1000 cc. of extract has been obtained. This is finally passed through a dry filter to free it from flocculent matter.

For the estimation, quantities of 100 cc. each of this solution, representing 5 grms. of flock, are transferred to white porcelain dishes and evaporated to dryness. The dry extract is heated sufficiently to just char the organic matter, cooled, a little water added and a few drops of potassium chromate solution, and the chlorine titrated with silver nitrate solution of the same strength as used in water analysis (1 cc. = 0·001 Cl). The final solution need not be filtered as the charred matter does not interfere with the end-point of the reaction. A minute quantity of pure lime may be added to the extract before evaporation to prevent loss of chlorine during the subsequent heating, but this is unnecessary if the heating is stopped short of actual ignition.

This method has been found to give accurate results when known quantities of sodium chloride have been added, and concordant results in duplicates.

In the case of unwashed flocks made from rags and old clothes it is advisable to add to the first water some suitable germicide, such as pure phenol.

Stepney, E.

THE CHEMICAL EFFECTS OF POLARISED LIGHT.

By E. G. BRYANT, B.A., B.Sc.

In many parts of the world, more especially in tropical regions, there is a widespread belief in the deleterious effects of moonlight on fish, and to a lesser degree on meat intended for food. This belief is by no means confined to sailors, fishermen, and other superstitious or ignorant persons. Many doctors are convinced of its truth—it has been officially given as the cause of death in at least one South African inquest; I have received some most trustworthy statements of the ill-effects produced in persons who had partaken of fish that had been so exposed. There are also closely allied beliefs as to the danger of sleeping with the tropical moon shining full on the face, the effects of moonlight on seeds, on growing plants, and the rising of the sap in wood.

It seemed to me that a possible explanation of these phenomena, supposing them to be true, might lie in the well-known fact that the light of the moon, being reflected light, is more or less polarised. I examined all the authorities at hand, but could find no reference to any work carried out on polarised light with reference to its chemical effects.

I therefore made an endeavour to test for any such effects, and this short note embodies the results I have been able to obtain. For one or two experiments I had the use of a 200 candle-power Osram lamp, but the others received only light from a 32 candle-power carbon-filament lamp. The light was polarised by means of a pile of seven sheets of plate-glass, backed with a silver mirror and placed at the correct angle. I hope to be able to continue the work with the larger lamp, as it is evident that no decisive results can be obtained without a fairly powerful beam of light.

The most marked results were obtained from fish. If two slices, cut from the same fish, were hung, one in the direct light, the other in the polarised beam, the latter invariably began to decompose before the former, though the temperature of the polarised beam was several degrees lower than the direct light. These experiments were carried out with the large lamp. Tests were arranged with the small lamp on meat, jam, cane-sugar solution

and several kinds of seeds. The sugar showed absolutely no change; of the others, none could be called decisive, but whenever any difference was observable it was always in favour of the polarised light.

Grey Institute,
Port Elizabeth, South Africa.

THE ACTION OF FINELY-DIVIDED NICKEL ON NITRIC OXIDE.

By R. S. FELGATE.

From thermodynamic considerations it might be expected that nitric oxide would be decomposed at ordinary temperatures when brought into contact with a suitable catalyst.

It is well known that finely-divided nickel when heated brings about the decomposition of the gas, and it has been found that cokernut charcoal cooled to the temperature of liquid air produces the same effect, yielding as final products carbon dioxide and nitrogen (Gray, "Ueber das Atomgewicht des Stickstoffs," Inaugural Dis., 1907).

It has now been found that the gas can be catalytically decomposed by finely-divided nickel suspended in hot water, the products being nitrogen and nickel oxide.

In a specially constructed glass apparatus pure nitric oxide, obtained by the fractionation of the liquefied gas and free from higher oxides, was caused to circulate through hot water containing in suspension finely-divided nickel, prepared by the reduction of the dry precipitated hydroxide in an atmosphere of hydrogen. The nickel was rapidly converted into the oxide, and the circulating gas on analysis was found to contain 20 per cent of nitrogen. After the experiment the filtrate from the suspended nickel was found to contain traces of ammonia (the amount found was no more than could correspond to the hydrogen occluded on the nickel), but since no appreciable amount of nickel was present in it and since the gas after the experiment contained no hydrogen, the possibility of the action from the presence of higher oxides is excluded. A similar experiment with colloidal nickel prepared from nickel electrodes by Bredig's method gave no result, but a third experiment with another sample of reduced nickel, prepared as described, confirmed the first result.

The action appears to depend upon the state of aggregation and method of preparation of the nickel catalyst, and further investigation of this point is proposed.

University College, London.

THE EFFECTS OF SULPHATES ON THE DETERMINATION OF NITRATES.

By W. P. KELLEY.

Introduction.

As is well known, the determination of nitrates in the sanitary analysis of water is generally made with the aid of the phenoldisulphonic acid reagent. During recent years this reagent has found extensive application in soil investigation, particularly in studies on nitrification. The chemistry of the reactions involved in this determination has been extensively studied, and, as shown by Chamot and Pratt (*Journ. Am. Chem. Soc.*, xxi., 922; xxxii., 630; xxxiii., 366), the yellow colour that is produced depends upon the formation of the tri-salt of the phenoldisulphonic acid. It is not the purpose of this paper, however, to discuss the chemistry of this reaction, but rather to present some data bearing upon the effects of sulphates on the nitrate determination.

Natural waters, as well as the solutions obtained from soils, frequently contain various salts. Among these are the chlorides, carbonates, and sulphates. The effects of chlorides and carbonates on the determination of nitrates have been studied in detail, especially the former; but the fact that the phenoldisulphonic reagent contains free sulphuric acid, which upon neutralisation gives rise to sulphates, has caused chemists to neglect to study the effect of sulphates.

Recently, Lipman and Sharp (*Univ. Cal. Pub. Agr. Sci.*, i., No. 2, pp. 21—37) published some investigations on this subject in which chlorides, carbonates, and sulphates were studied. They found, in common with previous studies, that chlorides caused an apparent loss of nitrates, but, contrary to previous observations, carbonates have no effect. They further found that considerable loss of nitrate took place upon evaporating a nitrate solution containing sodium sulphate. The addition of dry sodium sulphate to the dry nitrate residue, however, occasioned no loss of nitrate. From these observations the claim is made that sulphates cause a loss of nitrate in this determination, not by interfering with the phenoldisulphonic acid reaction, but by the expulsion of nitric acid during the time of evaporation on the water-bath. Hence they conclude that nitrate determinations in solutions containing sulphate must be made by the use of other methods.

As above stated, soluble sulphates are frequently present in soils. In addition it is a common practice to employ a solution of alum as a coagulating agent in order to secure clear soil solutions. While it is true the use of alum as a coagulating agent may well be objected to for other reasons, as pointed out by Lipman and Sharp, the suggestion that sulphates in general cause a loss of nitrate during the time of evaporation merits further study. The more especially is it important that this subject be investigated, since in the numerous nitrification studies now being carried on in many parts of the world, ammonium sulphate is often used as a source of nitrogen, and therefore soluble sulphate is bound to occur in the water extracts in which the nitrate determinations are usually made.

For some time the writer, at the suggestion of Mr. S. S. Peck, of the Hawaiian Sugar Planters' Experiment Station, has made use of calcium sulphate as a coagulating agent in the determination of nitrates in Hawaiian soils. This material has proven to be a most efficient coagulating agent with the abnormal soils of the Islands, often being found to be far more effective than calcium oxide or carbonate. In fact, the last named compounds cause a deflocculation in some of the heavy upland soils, while calcium sulphate brings about rapid coalescence of the finely divided particles, thus effectively aiding in securing a clear solution. On account of the extensive use that has been made of calcium sulphate in this laboratory it became necessary to test the effect of this compound on the nitrate determination. The results proved to be so out of harmony with the conclusions reached by Lipman and Sharp that a study of some of the more common sulphates was also undertaken.

Experimental.

The nitrate solution used in this work was prepared by dissolving in distilled water potassium nitrate at the rate of 250 parts of nitrogen per million, and portions of the solution containing the amounts of nitrogen shown in the subjoined tables were taken in all of the determinations reported in this paper. The sulphates were employed in solution prepared by dissolving 1 grm. in 1 litre of distilled water, and varying amounts were added to the nitrate solution, as shown in the tables. After evaporating on a water-bath, and cooling, the residues were treated with 2 cc. of the freshly prepared phenoldisulphonic acid reagent, allowed to stand five minutes, diluted to about 30 cc., and the colour developed by carefully adding strong ammonia until alkalinity was produced and a permanent colour obtained. After diluting to 250 cc., aliquot

portions were then used for making comparisons in a colorimeter with a standard nitrate solution prepared in the same way. All determinations were made in duplicate. The results follow :—

Effects of Sulphates on the Determination of Nitrates.

(0·275 mgrm. Nitrate Nitrogen Used in each Determination).

Sulphate added.	Na_2SO_4. Nitrate N found.	K_2SO_4. Nitrate N found.	$MgSO_4$. Nitrate N found.	$(NH_4)_2SO_4$. Nitrate N found.	$CaSO_4$. Nitrate N found.
Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.
None	0·275	0·275	0·275	0·275	0·275
1·00	0·275	0·280	0·272	0·237	0·270
5·00	0·265	0·270	0·277	0·203	0·270
10·00	0·225	0·210	0·270	0·235	0·273
20·00	0·180	0·265	0·275	0·225	0·273
40·00	0·140	0·260	0·277	0·225	0·280

It will be seen from the above data that when any considerable amounts of sodium, potassium, or ammonium sulphate were added considerable loss of nitrate took place, whereas neither calcium nor magnesium sulphate occasioned any loss. It will also be seen that the losses of nitrate from solutions containing sodium sulphate were roughly proportional to the amounts of sulphate present, and that important losses were sustained amounting to practically 50 per cent of the nitrate originally present when the larger amounts of the sulphate were used. On the whole the losses from potassium or ammonium sulphates were also proportional to the amounts used, but not so great as in the case of sodium sulphate.

The fact that neither calcium nor magnesium sulphate produced any effect on this determination, while the other sulphates caused losses of nitrate, led to a further investigation of the question. A new solution of sodium sulphate was prepared and used in the same way as above outlined. The results proved to be decidedly different from those previously obtained, the loss of nitrogen being very slight in any case. Subsequent trials showed it to be difficult to secure concordant results when sodium, potassium, or ammonium sulphate was employed, and that only when practically the same conditions of evaporation are maintained, such as the rate of evaporation, temperature, &c., were the results identical.

Lipman and Sharp hold that the loss of nitric nitrogen takes place during the time of evaporation, and consider the loss to be due to the expulsion of nitric acid, brought about by the combined action of heat and the sulphate radical. Theoretically, at the temperature obtained on the water bath no action should take place if the sulphate radical be completely combined in the normal sulphate combination. It was suggested, therefore, that probably the sodium sulphate contained small amounts of the acid sulphate, or that hydrolysis took place to a limited degree, resulting in the formation of small amounts of the acid sulphate.

With the view to throwing some light on this point varying amounts of sodium bisulphate were added to portions of the nitrate solution, evaporated, and the determinations completed as usual.

Effects of Sodium Bisulphate.

$NaHSO_4$ added.	Nitrate N added.	Nitrate N found.
Mgrm.	Mgrm.	Mgrm.
None	0·275	0·275
1·00	0·275	0·195
5·00	0·275	0·047
10·00	0·275	0·003
20·00	0·275	0·003
40·00	0·275	0·005

It will be seen that the acid sulphate under the conditions of these experiments can cause a relatively large loss of nitrates, 10 mgrms. having been found to expel practically all of the nitric nitrogen present. The loss was due to expulsion of nitric acid, as was shown by passing the vapours through a dilute caustic potash solution. Similar results were also obtained with other bisulphates. Therefore, acid sulphates, as might be expected, have the power of setting free nitric acid from nitrates during evaporation on the water-bath.

The expulsion of nitric acid by acid sulphates ought to be preventable by the addition of caustic alkali or carbonate. Experiments on this point showed such to be the case, if sufficient carbonate be added to the solution to completely convert the acid sulphate into normal sulphate. In the following series of experiments sodium carbonate was added to solutions containing different sulphates, and these then added to the nitrate solution, evaporated, and the determination completed as usual. The results are shown in the following table :—

Effects of Sodium Carbonate on the Loss of Nitrate N.

Sulphate added.		Sodium carbonate added.		Nitrate N added.	Nitrate N found.
	Mgrms.		Mgrm.	Mgrm.	Mgrm.
None	—		None	0·275	0·270
Na_2SO_4 ..	20		None	0·275	0·185
Na_2SO_4 ..	20		20·00	0·275	0·277
K_2SO_4.. ..	20		None	0·275	0·240
K_2SO_4.. ..	20		20·00	0·275	0·280
$(NH_4)_2SO_4$..	20		None	0·275	0·190
$(NH_4)_2SO_4$..	20		20·00	0·275	0·270
$NaHSO_4$ ..	20		None	0·275	0·006
$NaHSO_4$ ..	20		20·00	0·275	0·280
None	—		20·00	0·275	0·282

From the above data it is shown that sodium carbonate may prevent the loss of nitrates brought about by different sulphates just as would be expected if the loss is caused by the liberation of nitric acid.

In this connection it should be stated that Lipman and Sharp were unable to prevent the loss of nitrates occasioned by sodium sulphate by the addition of sodium carbonate. In the experiments reported above, however, the loss of nitrate during evaporation was entirely prevented by the addition of sodium carbonate. The experiments on this point have been repeated several times, and in no instance was any important loss of nitrate observed when an excess of sodium carbonate had been added to the solution. Indeed it seems difficult to believe that nitric acid could be volatilised and expelled from a carbonate solution under the conditions usually obtaining in this determination.

It is furthermore of interest that no loss of nitrate was observed from the use of sodium carbonate alone. As was pointed out by Chamot and Pratt (*Journ. Am. Chem. Soc.*, xxxiii., 25) carbonates may occasion slight losses of nitrates, due to mechanical causes such as effervescence produced by the reaction of the phenoldisulphonic acid reagent on the carbonates. If sufficient caution be observed, however, such losses may become negligible.

The data submitted in this paper indicate that the making of broad generalisations from specific instances may be entirely unwarranted. The fact that sodium sulphate (supposed to be none other than the normal sulphate) causes a loss of nitrate nitrogen, does not justify the sweeping conclusion that the sulphate radical in any inorganic combination would act in the same way. Although the evidence is of an indirect nature, the above data seem to justify the conclusion that losses of nitrate during evaporation in the presence of sulphates are probably referable to acid sulphates which were either originally present in the solution or perhaps formed by hydrolysis during the evaporation process. The latter view seems the more tenable, since losses took place only in the presence of the sulphates that most easily give rise to the bisulphate.—*Journal of the American Chemical Society* xxxv., No. 6.

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

Introduction.

THE investigation reported in this paper is a continuation of the work reported in a previous paper in which it was pointed out that "although it is well known that many of the methods which are generally used in qualitative analysis need revision, apparently very little time has been devoted to the systematic study of their relative effectiveness. It would seem, therefore, that any investigation which comprehended a detailed study of qualitative methods with particular reference to their accuracy in detecting small amounts of the elements in the presence of large amounts of any or all of the elements, and for the purpose of developing and formulating more reliable procedures, would be of considerable value to the analytical chemist." ("A Method for the Qualitative Analysis of the Calcium Group," Richard Edwin Lee and F. L. Mickle. *Orig. Com. 8th Intern. Cong. Appl. Chem.*, i., 257, 278; *Chem. Abstr.*, 1912, vi., 20, 3240; *Chem. Ztg.*, 1912, xxxvi., 1302.)

The purpose of this investigation, however, was the experimental survey of only those methods which are most frequently employed in the precipitation and separation of the metals of the zinc group, namely, zinc, manganese, nickel, and cobalt.

As in the investigation to which reference has been made, "it was hoped that the result of such an examination would render possible the selection of the best of the proposed methods and enable the formulation of the conditions best adapted to securing the desired end. As the work progressed, however, and larger discrepancies among the recommended procedures than had been anticipated were noted, it became obvious that although some methods ought to be revised, others ought to be rejected and new ones substituted, if possible."

Although an effort has been made to formulate such methods as will enable the analyst to estimate the approximate amount of the elements present, care has been exercised in the selection of the final procedures to adopt only those which may be executed with facility by the average worker.

The results of the investigation are reported in the order of their dependence. For convenience in presenting data, the paper has been divided into three parts: "Precipitation of the Group," "Analysis of the Group," and "Summary." Under each of the first two parts there is first presented a "General Discussion," in which the reasons for rejecting certain procedures, and adopting others, are given. This is followed by a record of the "Test Experiments" which were performed to test the accuracy of a given process. Next there is presented the "Procedure and Notes," in which the various details of the adopted procedure are submitted and briefly discussed.

The abreviations used in the cross references may be explained as follows:—G. D. is used for General Discussion; P. for Procedure; N. for Notes; T. E. for Test Experiments.

PART I.—*Precipitation of the Group:* (a) *General Discussion;* (b) *Test Experiments;* (c) *Adopted Procedure; Notes.*

(a) *General Discussion.*—With respect to the original precipitation of the members of this group, schemes of qualitative analysis differ as to whether this group and the preceding group (the Iron Group) should be precipitated separately by the successive addition of ammonium hydroxide and ammonium sulphide, or whether these reagents should be added together so that all the elements of the two groups may be obtained in a single precipitate. Authors are about evenly divided on this question of procedure. (Those in Group I. suggest the precipitation of the Iron Group with the Zinc Group; those in Group II., a separate precipitation for each group. Group I.: "Qual. Chem. Anal.," Noyes, A. A.; "Qual. Anal.," Dennis and Whittlesey; "Qual. Chem. Anal.," Noyes, Wm. A.; "Qual. Chem. Anal.," Treadwell, F. P.; "Qual. Chem. Anal.," Stieglitz, Julius; "Qual. Anal.," Baskerville and Curtman; "Anal. Chem.," Menschutkin, N.; "Qual. Chem. Anal.," Perkin, F. M. "Group II.: "Qual. Anal.," Böttger, W.; "Qual. Chem. Anal.," Tower, O. F.; "Qual. Chem. Anal.," Newth, C.; "Qual. Chem. Anal.," Bailey and Cady; "Qual. Anal.," Morgan, W. C.; "Qual. Anal.," Gooch and Walker; "Qual. Anal.," Hill, Arthur E.; "Anal. Chem.," Long, J. H.; "Qual. Chem. Anal.," McGregory, J. F.)

Either method has its advantages as well as its disadvantages. When the two groups are precipitated simultaneously, the problem of the analyst is exceedingly difficult, if large quantities of many of the metals of the two groups are present, and especially so if but traces of only one or two of the members are present. Again, zinc, aluminium, and chromium cannot be completely separated from manganese and iron by alkali hydroxide (Ebler, E., *Z. Anal. Chem.*, xlvii., 665–667; cf. *Chem. Abs.*, 1909, iii., 294—5), the reagent usually employed for this separation when the two groups are precipitated together. Finally, the colour changes which occur during the precipitation of either group and which frequently supply indications as to the presence or absence of certain metals, are partially or wholly obscured when the two groups are precipitated simultaneously.

The objections usually urged against the precipitation of each group separately is that it is difficult to effect a complete separation of the two groups. This difficulty may be nearly overcome by avoiding the use of an unnecessary excess of ammonium hydroxide when precipitating the iron group; or the more elaborate formate, benzoate, or basic acetate methods may be used. If the latter method is employed, phosphates are removed during the regular course of the analysis. Finally, the separate precipitation of the groups renders the analytical problem less complex.

It has seemed advisable, therefore, to adopt the method of precipitating the iron and zinc groups separately.

The next problem presented was the determination of the most reliable group precipitant, *i.e.*, whether ammonium polysulphide, ammonium monosulphide, or hydrogen sulphide should be used. An examination of many of the recommended schemes of analysis revealed the fact that the majority of authors prefer to precipitate the group by use of the reagent "ammonium sulphide." The work conducted in this laboratory, however, indicates that precipitation is most satisfactorily accomplished by hydrogen sulphide. Ammonium polysulphide, $(NH_4)_2S_x$, was rejected for two reasons: First, the sulphides of some of the members of the group, especially nickel sulphide, are markedly soluble in this reagent; second, its presence in the filtrate (from this group) imparts a deep yellow colour and in the subsequent analysis results in the separation of sulphur on standing or heating.

Ammonium monosulphide, $(NH_4)_2S$, as the group precipitant yielded fairly satisfactory results. However, the following objections may be offered to its use: First, nickel is very frequently precipitated in the colloidal condition; second, the shelf reagent, unless freshly made, is a constant source of difficulty, as the monosulphide is readily oxidised in the presence of air to the polysulphide, thus:

$$2(NH_4)_2S + O \rightarrow (NH_4)_2S_x + 2NH_3 + H_2O.$$

Therefore, if a large excess of the reagent is used it is practically equivalent to using the polysulphide.

The method of passing hydrogen sulphide, H_2S, into a weak ammoniacal solution containing the metals of this group presented no new difficulties and practically eliminated the difficulties attendant upon the use of either one

* *Journal of the American Chemical Society*, xxxv., No. 5.

of the two other precipitants. The dissolving of the nickel sulphide is entirely prevented and nickel is seldom precipitated in the colloidal condition.

It would seem, therefore, that the method of precipitating the group with hydrogen sulphide is to be preferred, especially so when nickel is likely to be present. By the procedure outlined in this paper (see Procedure I.) it is easily possible to precipitate as well as detect 0·0005 grm. of any of the metals of this group.

(b) *Test Experiments* (see Note). Series I.—Difficulties Encountered in Attempting to Precipitate Nickel by Ammonium Polysulphide or Monosulphide.

(Note.—The record of the "Test Experiments and References" is presented before the adopted procedure is reported. Conclusions drawn from the results obtained in the Test Experiments are incorporated in the "Procedure and Notes.)

After a few trial experiments with $(NH_4)_2S_x$ this reagent was rejected as a possible group precipitant because of its solvent action on nickel sulphide.

When large or small amounts of the pure salts of nickel were used in the test experiments, the complete precipitation of the nickel by the use of ammonium sulphide was found to be almost impossible. The filtrate invariably had a brown colour in each case. When it was boiled for five or six minutes, shaken thoroughly, and then filtered, it usually came through colourless. The amount of nickel in the filtrate apparently increased with the amount of $(NH_4)_2S$ used and the length of exposure to the air.

Lecrenier (*Chem. Ztg.*, 1889, xiii., 431—449), and Villiers (*Compt. Rend.*, 1894, cxix., 1263) have shown, however, that nickel can be completely precipitated as NiS—the filtrate remaining colourless—with freshly prepared $(NH_4)_2S$ in the absence of air. The results obtained by these men indicate that, in those cases to which reference has been made, the brown coloured filtrate is due to the presence of a polysulphide. The composition of this brown coloured filtrate, however, is probably not definitely known. It may be colloidal nickel polysulphide or it may be ammonium sulphonickelate, $(NH_4)_2NiS_3$. Antony and Magri (*Gazz. Chim. Ital.*, 1901, xxxi. [2], 265) prepared NiS_4 by evaporating the brown coloured filtrate in the absence of air.

All the experimental work relating to precipitation of the group with ammonium polysulphide or monosulphide showed that these reagents as possible group precipitants should be rejected.

Series II.—Completeness of Precipitation of Zinc, Manganese, Nickel, and Cobalt in an Ammoniacal Solution with Hydrogen Sulphide.

In the following series of experiments the amount of the metal in the form of a chloride was dissolved in distilled water and diluted to 25 cc., 5 cc. of 5N HCl was added, after which the solution was made *slightly* alkaline with 5N NH_4OH. Precipitation from both cold and hot solution was tried.

A. *Zinc.*

0·0003 grm. Zn (as $ZnCl_2$) gave no precipitate.
0·0004 grm. Zn (as $ZnCl_2$) gave no precipitate but the solution became turbid.
0·0005 grm. Zn (as $ZnCl_2$) gave a distinct precipitate after 1—2 minutes which coagulated perceptibly.
0·001 grm. Zn (as $ZnCl_2$) gave heavy flocculent precipitate.
0·200 grm. Zn (as $ZnCl_2$) gave large precipitate at once and precipitation was complete in 2—3 minutes.

B. *Manganese.*

0·0003 grm. Mn (as $MnCl_2.4H_2O$) gave no precipitate.
0·0004 grm. Mn (as $MnCl_2.4H_2O$) gave no precipitate but the solution became turbid.
0·0005 grm. Mn (as $MnCl_2.4H_2O$) gave a distinct precipitate.
0·001 grm. Mn (as $MnCl_2.4H_2O$), a distinct precipitate was obtained after 1—2 minutes.
0·200 grm. Mn (as $MnCl_2.4H_2O$) gave a heavy precipitate at once and precipitation was complete in 2—3 minutes.

C. *Nickel.*

0·0001 grm. Ni (as $NiCl_2.6H_2O$) gave only a slight colouration.
0·0002 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate which coagulated perceptibly.
0·0003 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·0004 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·0005 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·001 grm. Ni (as $NiCl_2.6H_2O$) gave a heavy precipitate at once.
0·200 grm. Ni (as $NiCl_2.6H_2O$) gave a heavy precipitate at once and precipitation was complete in 2—3 minutes.

D. *Cobalt.*

0·0001 grm. Co (as $CoCl_2.6H_2O$) gave no precipitate but solution became turbid.
0·0002 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0003 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0004 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0005 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·001 grm. Co (as $CoCl_2.6H_2O$) gave a heavy precipitate at once.
0·200 grm. Co (as $CoCl_2.6H_2O$) gave a heavy precipitate at once. Precipitation was complete in 2—3 minutes.

This series of experiments shows that quantities as small as 0·0005 grm. of either Zn, Mn, Ni, or Co are precipitated in 2—3 minutes. It is evident, therefore, that the method outlined in Procedure I. provides for a practically complete precipitation of the members of the group.

(c) *Procedure Adopted and Notes. Procedure* I. To the neutral acid solution (or the filtrate of Group III.) containing the elements of the Zinc Group, add 5N NH_4OH until the solution reacts slightly alkaline. Warm the solution, pass H_2S into it for five minutes, shake the mixture and again warm it. Filter at once. Test the filtrate with H_2S to ascertain whether precipitation is complete. If the filtrate has a dark brown colour the presence of colloidal nickel sulphide is indicated. This difficulty may be overcome by boiling this filtrate for 5—10 minutes. This operation coagulates the precipitate, and therefore prevents it from passing through the filter. The nickel sulphide may then be filtered without further difficulty. Wash the group precipitate immediately and thoroughly with an aqueous solution of H_2S. Proceed with the analysis without delay, as the moist sulphides of nickel and cobalt are easily oxidised.

Notes.

(1) If $(NH_4)_2S$ is used to precipitate the group, it mus be freshly prepared, as it oxidises in the presence of ai to ammonium polysulphide, in which it has been shown that NiS is soluble (see T. E., Series I.). The use of a large excess of the reagent $(NH_4)_2S$ is equivalent to the use of ammonium polysulphide.

If hydrogen sulphide is passed into the solution which is made slightly alkaline with 5N NH_4OH all of the difficulties enumerated are overcome and no new difficulties are presented.

(2) A large excess of ammonium hydroxide is to be avoided when the solution is made slightly alkaline preparatory to its treatment with H_2S, as the excess will be converted into $(NH_4)_2S$ and probably into $(NH_4)_2S_x$. On the other hand great care must be exercised to keep

the solution slightly alkaline in reaction during the precipitation with H_2S.

(3) It has been shown (T. E., Series I.) that the brown coloured filtrate is due to the presence of $(NH_4)_2S_x$, which exerts a solvent action upon NiS. This colloidal nickel salt may be coagulated by boiling and shaking and then removed by filtration.

(4) Precipitations from cold ammoniacal solutions were as satisfactory as those from warm solutions if the amounts of the metals were greater than 0·001 grm.

(5) The precipitation of the metals of this group is practically complete (see T. E., Series II.).

(To be continued)

ON THE

PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS.*

By LEROY MCMASTER.

MOST of the ammonium salts of organic acids described in the literature consist of a molecule of the ammonium salt combined with a molecule of the free acid in the case of monobasic acids, while, in the case of dibasic acids, the ammonium salt described is generally an acid ammonium salt. They were usually prepared by neutralising an aqueous solution of the acid with ammonium water or ammonium carbonate, and the solution allowed to evaporate to crystallisation. Many of the salts thus formed also contained water of crystallisation.

In attempting to prepare some diammonium salts by the above method, Keiser and McMaster (*Am. Chem. Journ.*, xlix., 84) always obtained the acid salts. They then dissolved the organic acids in absolute alcohol or ether and conducted into the solution a stream of dry ammonia gas. White crystalline salts were precipitated. In this manner they prepared the ammonium salts of fumaric, maleic, mesaconic, and citraconic acids, which, upon analysis, proved to be the diammonium salts. Ammonium salts of malonic acid and *o*-phthalic acid were also prepared, but were not analysed.

I have continued this work on the dibasic acids, and have prepared the neutral ammonium salts of malonic, succinic, malic, tartaric, *o*-phthalic, and *m*-phthalic acids. The method was applied also to the preparation of the ammonium salts of some monobasic acids—propionic, isobutyric, palmitic, benzoic, and cinnamic. Some of the properties of these ammonium organic salts have also been studied. All of the acids used were obtained from Kahlbaum, except the tartaric acid, which was Baker's analysed product.

Ammonium Malonate.—Finkelstein (*Liebig's Ann. Chem.*, cxxxiii., 338) attempted to make the neutral ammonium salt of malonic acid by adding an excess of ammonia water to an aqueous solution of the acid, and allowing the mixture to evaporate over lime. The liquid lost ammonia, and finally became acid. The acid ammonium salt crystallised out. I have prepared the neutral salt of malonic acid by the method described by Keiser and McMaster, but with some difficulty. If ammonia gas is conducted into an ethereal solution of the acid until no further precipitate is formed, the salt will be found not to be neutral. Analysis of two samples of the salt thus prepared gave respectively 16·65 per cent and 16·62 per cent of nitrogen. The acid ammonium salt of malonic acid contains 11·57 per cent of nitrogen, and the neutral salt 20·29 per cent nitrogen. It is thus evident that each of these preparations was a mixture of the acid ammonium salt and the neutralt salt. In this experiment dry ammonia was conducted into an ethereal solution of 5 grms. of malonic acid for about one half-hour. However, if the ammonia is run into a solution of 5 grms. of malonic acid for about three hours and allowed to come in contact with the precipitated salt, the neutral ammonium malonate is formed. The salt thus prepared is a white crystalline powder, not deliquescent but readily soluble in water. The aqueous solution is neutral. The salt, on analysis, gave the following results :—

N calculated for $CH_2(CO_2NH_4)_2$	20·29
Found—I.	20·3
II.	20·26

The first nitrogen determination was made by the Dumas method, the second by the Kjeldahl method.

Ammonium Succinate.—Berzelius states in his *Lehrbuch der Chemie* that the salt which results from the evaporation of a neutral solution of ammonium succinate is an acid salt. By adding an excess of ammonia to a solution of succinic acid and allowing the liquid to evaporate, Doepping (*Liebig's Ann. Chem.*, xlvii., 253) obtained a salt that was easily soluble in alcohol, and not deliquescent. He concluded that he had a neutral salt. Fehling (*Ibid.*, xlix., 154) found that the neutral salt could not be so easily prepared, and that the salt obtained by the method of neutralisation and evaporation is either an acid salt or a mixture of the acid and neutral salts, especially if ammonia is used in excess. He obtained the neutral ammonium salt by adding to basic lead acetate an excess of a solution of neutral ammonium succinate and evaporating in a vacuum over sulphuric acid the mother-liquor. As soon as the mass was mostly crystallised out, it was washed with a little water to remove traces of lead, pressed between filter-paper, and dried at 40—50°. Fehling thus obtained the neutral ammonium succinate in crystalline form.

Dry ammonia gas was run into an alcoholic solution of succinic acid, and a white crystalline powder was formed which was not deliquescent in the air but dissolved readily in water. The aqueous solution was neutral to sensitive litmus-paper. The salt is only very slightly soluble in alcohol, and was washed on the filter with alcohol and ether. The salt can also be prepared by conducting the ammonia into an ethereal solution of succinic acid. The salt prepared in absolute alcohol gave, on analysis, the following results :—

N calculated for $(CH_2CO_2NH_4)_2$.. ..	18·42
Found—I...	18·36
II...	18·38

Prepared in ether :—

N found	18·38

Ammonium Malate.—No record can be found of the preparation of neutral ammonium malate. The acid malates have been made and extensively studied by Pasteur (*Liebig's Ann. Chem.*, lxxxii., 331) and Bremer (*Ber.*, xiii., 352). When ammonia gas is run into an alcoholic solution of malic acid, there is first formed a white mucilaginous substance which soon changes to a crystalline powder. Analysis proved this salt to be a mixture of ammonium acid malate and the neutral malate. The neutral salt was prepared by passing the gas into a solution of 5 grms. of the aid for several hours, the salt filtered off by suction, washed with alcohol and ether, dried in a desiccator, and then placed in a dry flask, filled with ammonia, and tightly stoppered. The flask was shaken at intervals, and portions taken out from time to time and tested for neutrality. It was found necessary to allow the salt, prepared as described above, to stand in contact with the ammonia for three days in order to become neutral. The compound thus prepared was very slightly deliquescent, and dissolved readily in water. Determinations of nitrogen by the Kjeldahl method gave :—

* Presented before the St. Louis Academy of Science, February 17, 1913. From the *American Chemical Journal*, xlix., No. 4.

N calculated for $C_4H_4O_5(NH_4)_2$	16·66
Found—I...	16·64
II...	16·63

Ammonium Tartrate.—Tartaric acid was dissolved in absolute alcohol and ammonia gas passed into the solution until a portion of the salt on being dissolved in water showed a neutral solution. When the ammonia was first passed in a white curdy precipitate formed. This soon changed to an amorphous powder which, as soon as neutral, was filtered by suction on an alundum crucible, and washed with alcohol and ether. The salt is not at all deliquescent, and is very slightly soluble in alcohol. Analysis gave the following result:—

N calculated $C_4H_4O_6(NH_4)_2$..	15·21
Fonnd	15·19

Ammonium o-Phthalate. — Marignac (*Liebig's Ann. Chem.*, xlii., 215) describes the preparation of this salt by the action of liquid ammonia on the acid. This salt was precipitated from an alcoholic solution of *o*-phthalic acid by dry ammonia, filtered by suction on an alundum crucible, washed with alcohol and ether, and dried in a desiccator. It is a fine white powder, soluble in water, scarcely soluble in alcohol. The salt is not deliquescent.

N calculated for $C_6H_4(CO_2NH_4)_2$ . ..	14·00
Found	13·98

(To be continued).

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Toxic Fish with Venomous Milts.

Although venomous fishes have long been known, what are much less known are those whose glands contain poisons capable of provoking poisoning, and that only at a certain period of the year. Since 1882 Russian and Japanese doctors have taken up this question, after having observed symptoms of poisoning after the ingestion of fish coming from the coast of Nippon and belonging to the species *Tetradon* and *Orthagoricus*. The toxins are in the head, liver, and especially the milts and roes of these fish; while the flesh is absolutely inoffensive and may be consumed without the slightest inconvenience. The toxic effect seems to be specially localised in the ovaries and testicles of these fish, other species of which are to be found in the waters of the Cape and New Caledonia. The venomous matter does not exist on account of the putrefaction of these organs, which are toxic even when in an absolutely fresh state. Several observations of poisoning have been reported from the ingestion of certain fish of Asiatic rivers, the glands of which as well as the flesh, when once ingested, bring on gastro-intestinal troubles, collapse, and death. The flesh becomes inoffensive after cooking, whereas the eggs and the milt remain toxic after lying six months in alcohol. The toxin of the *Tetradon* is principally to be found in the ovaries, and this explains the frequency of the accidents during the spawning season in April and May. The toxin paralyses the animals experimented upon and appears to have a particular affinity for the bulbous centres. It does not seem to be an organised ferment nor an inorganic base. In fact all the searchers are agreed as to the seat of this poison; the liver and the testicles are generally less toxic than the ovaries, and the muscles rarely contain any noxious principle. Heat can destroy this toxin, but the ebullition must be prolonged for three hours at least to obtain its perfect destruction. At the time of spawning there is normally a special morbid alteration that is the veritable cause of the poisonous nature of the glanduary organs of these fishes. The maximum of toxicity coincides with the maximum of the activity of the glands. This phenomenon is analogous to that observed in the muscles of overtaxed animals; the muscles of hunted animals become real poisons. Up till now no poisonous fishes have been met with on the coast of France. The accidents that have been observed in Europe after the ingestion of fish were due either to a state of putrefaction or to the bacillary infections of these animals.

M. A. J. Albahary has made most interesting researches on this subject, but it would be interesting if analytical chemists were to try and determine in a precise manner the nature of this noxious and venomous principle in the glands.

Dwarf Plants and Monstrous Flowers.

M. J. A. Urbain, Professor of Chemistry at the Sorbonne, has had the idea of making seeds germinate after having deprived them of their albumen. Thus, by his own will, he obtains monstrous vegetables. His work is returned in a paper read before the Academy of Sciences by the eminent Professor of Botany, M. Gaston Bonnier. Evidently the albumen of a seed is not its essential part; albumen is only an alimentary reserve destined to feed the young plant until its radicle has become strong enough to seek for its food itself. But can the young plant do without this alimentary reserve? M. J. A. Urbain shows that, if put to the test, it can do so, but not without suffering from the privation. M. Urbain's experiments have been made with seeds of the Palma Christi, the poppy, &c. These seeds deprived of their albumen germinated like normal seeds, but produced dwarf, stunted plants with modified leaves and often monstrous deformed flowers. This research of M. Urbain goes to prove the possibility of creating monstrous plants at will. In the same way way the late Camille Daresle produced, at will, monstrous chicken by interfering with the normal evolution of the egg, either by varnishing a part of its surface, or by exposing it to a too strong heat, or by tormenting it in some other manner.

The Microbe of Hydrophobia Discovered.

A discovery of extreme importance, which will mark its date in the history of bacteriology, has just been made by Prof. Hideyo Noguchi, the learned Japanese who has made so many researches concerning syphilis. Noguchi has just simply discovered the invisible microbe of hydrophobia. In an article just published in the *Presse Medicale* the learned Japanese describes the method that has enabled him to see the nucleated round or oval corpuscles that seem to be the infectious agents of hydrophobia. Galtier and Pasteur have shown that hydrophobia is infectious. Other learned men, as Remlinger, Volpino, Poor, Steinhardt, have shown the filtrability of the virus of rabies, but the nature of the virus itself had remained unknown. It was in the beginning of 1912 that Noguchi undertook the culture of the virus of rabies. He has made about fifty series of cultures with the brain or the marrow taken aseptically from rabbits, guinea-pigs, and dogs to whom the virus of rabies had been transmitted. In these cultures he reproduces the tiny granulous corpuscles of the hydrophobic virus which are to be found at the limit of microscopic visibility. The method employed to cultivate these infinitely small microbes and to render them visible is that which has been employed for the culture of the spirochetes of recurrent fever. The appearance of these corpuscles was sudden and abundant and of a duration of four or five days. These cultivated corpuscles do not look like bacteria but like protozoa. Noguchi has made his controlling experiments at the Rockefeller Institute of New York, where he has his laboratory. With the cultures containing these granulous corpuscles he has inoculated dogs, rabbits, and guinea-pigs, who all in a short time showed the typical symptoms of rabies. Prof. Noguchi's discovery will throw a new light on the very obscure problem of filtering microbes, and open new horizons to bacteriological science.

WIRELESS TELRGRAPHY STATIONS.

At the present moment there exist on the surface of the globe 230 radiotelegraphic stations open to the public; they are to be found in the following places:—Canada 32, England 25, Russia 22, Germany 20, Italy 20, Brazil 16, East Indies 11, Spain 9, and France only 8. Over the different seas of the globe 1200 mercantile vessels are navigating provided with wireless telegraphy. Here, again, France with 90 vessels comes far behind England (590) and Germany (253). The majority of French ships provided with apparatus for free communication belong to the two ports of Marseilles (46) and Havre (29). However, it is to be remarked that Marseilles, although possessing more than half the ships provided with wireless telegraphy apparatus, has, as yet, no central station, and from this point of view is tributary to the station of Sainte-Marie-de-la-Mer, from whence the radio-telegrams are transmitted by telephone. To indicate the development of this new mode of communication and the necessity of endowing Marseilles with a central station it suffices to give the number of messages received: 22 in 1908, 2393 in 1910, 6151 in 1911, 8217 in 1912. These figures are sufficient without further comment.

THE LAST TWO COMETS.

M. Chauffardet, of Besançon, has just made a study of the last two comets that approached our world in 1913. The last is quite recent. Russian astronomers took it for a planet of the eleventh magnitude, and thought they had made a fine discovery. It was, however, a false joy. It was an old acquaintance—a periodical comet that has come to visit us for the third time since 1889. Its periodicity is then only of eight years. This, for a comet, is but a very small orbit, which accounts for its having been taken at first for a planet. The mistake is explained by the presence of a very small nucleus with very distinct outlines, and which was visible before the appearance of the tail.

THE OLFACTORY SENSE OF INSECTS.

A great number of facts of the life of insects can hardly be explained excepting by admitting a particularly powerful olfactory sense in these animals. The examples are numerous; if, in an ant hill, an ant of the same species as those that inhabit it, but belonging to another swarm, tries to penetrate, it will immediately be expelled. Sometimes the hypothesis has been supposed of a sort of language allowing each individual to make itself known, but deafness is general in the class of insects, and ants in particular are absolutely deaf. So then there only remains the odour special to each swarm which appears to conetitute a mode of identification. In the same way, when the corpse of a small mammiferous animal is becoming decomposed in a field, a legion of sylphs and necrophors, strangers to the immediate neighbourhood, coming sometimes from a distance of several kilometres, arrive to lay their eggs there, guided, it would seem, merely by their sense of smell. It is also their scent which leads the sacred scarabeus to the excrements of herbivorous animals, of which it will make a ball in which to place its progeniture, &c. But is it really scent that guides the insect? Very little is known on the subject; the only precise experiments are due to Fabre, the learned entomologist of Serignan, to whom are due those marvellous studies on the life of insects that he has so well related in his "Entomological Mémoires." The starting-point of these experiments was the sexual attraction in butterflies, well known to entomologists, which enables individual insects to meet in spite of the often considerable distance and difficulties of the way. Fabre enclosed females of different species of butterflies in a metallic trellis, and found that numerous males arrived. A remarkable particularity of these experiments was that one of the specimens studied had very rarely been observed in the region. On the contrary, if the females were shut up under an hermetically closed glass globe the attraction ceased, but all objects, branches, stuff, paper, on which they had rested for some time was seen to be possessed of the same attractive properties. Fabre has concluded from these results that a particular odour exists incapable of affecting our sense of smell, but which can be transmitted to a great distance. Although it is bold to generalise, it seems possible to admit that insects are endowed with a wonderfully strong olfactory sense which no other animal possesses.

ERNEST SOLVAY AND SODA.

The Jubilee of Ernest Solvay that has just been celebrated in Belgium has drawn attention to one of the most important chemical industries—that of soda. J. B. Dumas said that the two greatest novelties of the nineteenth century were the steam-engine and artificial soda, which may be considered as the staff of chemical industry. A century ago soda was obtained by the calcination of certain plants, and Spain, who was the greatest producer, exported into France more than 30 millions of soda. But in 1793 the blockade closed all the French frontiers, and the want of Spanish soda was so strongly felt by French industry that the Republic made an appeal to all citizens who had establishments, or who had obtained patents, for obtaining soda from sea salt. Nicholas Leblanc's process was seen to be the only practical one, and the inventor generously and patriotically made his invention public. This saved French industry, but poor Leblanc was ruined, and losing his wits through distress and poverty he committed suicide. Eighty years later 500,000 tons of soda, worth 80 millions of francs, were manufactured annually by his process! It was accidentally in mixing carbonate of ammonia with sea salt, that Solvay noticed the formation of soda. He patented the process in 1861, but it was only in 1865, after the invention of the carbonator column, that the process became profitable and made the fortune of its inventor. In 1865 the factory of Couillet produced 400 kilogrms. of soda a day, 1500 kilos. in 1866, and 3000 in 1867. Since that time the production by the Solvay method has steadily increased. In France, in 1875, the enormous factory at Dombasle was established, producing 250,000 kilogrms. a day. Then came the manufactories of Sandbach in England, of Wylen and Bernbourg in Germany, of Bereneski in Siberia, and Syracuse in America, which employ 800 directors and 12,000 workmen. The Solvay factories produce 1,700,000 tons of soda a year out of a total mundane consumption of 1,800,000 tons. Thanks to this process the price of soda has gone down from £5 a ton in 1860 to 24s. in 1868 and 10s. in 1882.

NOTICES OF BOOKS.

Water Purification and Sewage Disposal. By Dr. J. TILLMANS. Translated by HUGH S. TAYLOR, M.Sc. London: Constable and Co., Ltd. 1913.

THIS critical survey of modern methods of water purification and sewage disposal deserves a warm reception at the hands of sanitary authorities in England, who will find that in all respects it is thoroughly up to date. The purification of drinking water on the small and large scales is first discussed, and the advantages and disadvantages of different methods are clearly and concisely exhibited. Various processes for water softening for technical purposes are considered in a short chapter. The purification of sewage by biological and other means is then described, and the disposal of industrial sewage is fully treated. The effluents of some thirty different industries are considered separately and in some detail, and the results of recent investigations are discussed.

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, et de Technologie. ("Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological"). Paris: Gauthier-Villars. London: J. and A. Churchill. 1913.

Very few alterations have been found necessary in this second volume of numerical tables beyond bringing all information down to the latest possible date. The data included in the chapter on the Properties of Mixtures have now been distributed in suitable places throughout the text, and in some cases English weights and measures have been replaced by those of the metric system. The explanations are usually in French, but the indexes and titles are printed in English, French, German, and Italian, and technical and collegiate libraries in these four countries will find the book invaluable.

Forty-ninth Annual Report on Alkali, &c., Works. By the Chief Inspector. London: His Majesty's Stationery Office. 1913.

The forty-ninth annual report on alkali, &c., works contains the detailed reports of the work of the district inspectors, together with a discussion of them by the Chief Inspector. The number of registered works in the country shows a net increase of 9, and on the whole the chemical industry exhibited great activity during the year 1912. The report also contains further details of the investigation of the behaviour of oxide of iron during fouling and revivification, which was considered at some length in the preceding report.

The Cane-sugar Factory. By Frederic J. Scard, F.I.C. London: The West India Committee. 1913.

This little book provides, at a very moderate price, a brief guide to the processes of milling, clarification, filtration, &c., employed in a cane sugar factory. It is written in the form of question and answer, and the study of it will excellently prepare the beginner for the use of more advanced works. While no attempt is made to go deeply into scientific principles, the practical methods employed are clearly outlined, and a complete glossary of the terms used in cane-sugar practice is given, together with some useful numerical tables, including a concentration table showing the percentage of water evaporated between given densities.

An Investigation of the Coals of Canada. By J. B. Porter, E.M., D.Sc., and R. J. Durley, Ma.E. Vol. VI. Ottawa: Government Printing Bureau. 1912.

The sixth volume of the report of the investigation of Canadian coal which has been conducted at the McGill University, Montreal, contains Appendix IV. on the manufacure and testing of coke, and Appendix V. on the work of the chemical laboratory. In the latter details are given of the analyses of coal samples undertaken in the laboratory, and some weathering tests are described. A paper on the spontaneous combustion of coal by Dr. E. Stansfield, M.Sc., read before the Canadian Mining Institute is also reproduced. It contains a summary of the literature of the subject down to the year 1910, and discusses some cases of spontaneous combustion which have occurred, and also the remedial measures which have been or may be adopted.

E. Merck, Chemical Works, Darmstadt, Germany. London: E. Merck, 66, Crutched Friars. July, 1913.

The name of Merck is now fully recognised as a guarantee of the purity and absolute reliability of a chemical, and the firm has always been in the vanguard in the manufacture of all classes of pharmaceutical preparations. In the latest list of chemicals one of the most important additions is Fibrolysin, a remarkable solvent for scar tissue, which is now quoted for the first time.

Graham Flour. By J. A. Le Clerc and B. R. Jacobs. Washington: Government Printing Office. 1913.

This *Bulletin* of the Bureau of Chemistry of the U.S. Department of Agriculture contains the Report of a careful study of the differences between the physical and chemical properties of true and imitation Graham or whole-wheat flour. The authors have found that many millers have long been in the habit of making a so-called Graham flour by mixing low grade flour and bran in suitable proportions, and by a great number of comparative experiments with different samples they have discovered what determinations must be made in order to ascertain whether a given flour is genuine or otherwise. These determinations relate chiefly to the quantity and character of the intermediate products and to the amounts of fibre, ash, and pentosan, which are always less in imitation than in true Graham flours.

Gas Analysis. By L. M. Dennis. New York: The Macmillan Company. 1913.

The text of this book is based upon the English translation of Hempel's "Methods of Gas Analysis," but it is practically a new work, for the great advances in methods of analysing mixtures of gases which have been made during the last few years, and the many new pieces of apparatus which have been devised for special purposes, are all duly described. The processes included for description are chiefly those which are useful in rapid technical analysis. General methods and the manipulation of gases are treated fully in the early part of the book, and a chapter on the construction of apparatus contains practical hints which will be of great value to those who are not experienced in work of this kind. The theory and practice of the determination of gases by combustion are well explained, and de Voldere and de Smet's laws of the combustion of gases are summarised. The properties and determination of the various gases which are of technical importance and of mixtures of them are then described, and the analysis of atmospheric air, illuminating gas, &c., is discussed in detail.

Protection of Intellectual Property. By Dr. L. H. Baekeland.

This pamphlet contains the Presidential Address, delivered by Dr. Baekeland before the Meeting at Detroit of the American Institute of Chemical Engineers in December, 1912, which has been reprinted from the *Journal of Industrial and Engineering Chemistry*. In it Dr. Baekeland puts forward an eloquent plea for the need of widening the Patent Laws and educating the public in a rational and equitable view of the importance of the reform of the whole patent system. He takes into consideration chiefly chemical patents, as being the most difficult to protect from infringement, and although he claims that on the whole the American Patent Laws are the best, he has many suggestions to offer for improving them. The Oldfield Bill he regards as likely to have far-reaching and dangerous effects. Possibly the most valuable of his proposed improvements is based upon the German system, by which the burden of technicalities and expert knowledge is thrown upon the Patent Office, or a Court connected with it, which with a Court of Appeal would constitute an efficient machinery for adjudicating the title and validity of patents, lessen the cost of administrating the laws, and encourage a healthy inventive activity among poor men as well as those who have large means at their disposal.

L'Année Electrique. ("The Electrical Year"). By Dr. Foveau de Courmelles. Paris: Ch. Beranger. 1913.

This book contains a review of progress in electricity, electrotherapy, and radiography during the year 1912. A great many results are brought together in it, especially

as regards the medical use of electricity, while recent advances in the applications of electricity in traction, lighting, &c., are shortly described. Those who want a semipopular account of electrotherapy will find it in the book, which also gives full references to periodical literature on the subject.

Cours Élémentaire de Chimie et de Minéralogie. ("Elementary Course of Chemistry and Mineralogy"). By Dr. C. I. ISTRATI and Dr. G. G. LONGINESCU. Second French Edition. Translated by A. ADAM. Paris: Gauthier-Villars. 1913.

THE inductive method of learning chemistry is advocated in this book, which will give the student a satisfactory grounding in the subject, and enable him to profit by the subsequent use of more advanced works. In the early chapters the authors proceed always from the known to the unknown, and the consideration of the atomic theory is deferred until the student has acquired a fair knowledge of some of the common elements and their more important compounds. On the other hand, the deductive method is not altogether discarded, but is effectively employed in the latter part of the book which deals with organic chemistry. Many experiments, mostly such as are easy to perform with simple apparatus, are described, and technical applications are in many cases given some prominence. A good deal of attention is paid to mineralogy, and the book is wonderfully comprehensive, containing a large amount of matter which is logically presented to the reader and thoroughly well arranged.

Einführung in die Spektrochemie. ("Introduction to Spectrochemistry"). By G. URBAIN. Translated by Dr. ULFILAS MEYER. Dresden and Leipzig: Theodor Steinkopff. 1913. (Mk. 9).

THE most important facts and theories of elementary spectrochemistry are very well summarised in this book, and Prof. Urbain has at his command a lucid and graphic style which should be much appreciated by those who are beginning the study of the subject. The elementary theory of light and the formation of the spectrum are treated in introductory chapters, which lead up to a detailed account of the technique of the production of spectra. Many diagrams of apparatus are reproduced, and full descriptions of experiments are given. The theory of electrochemistry is also shortly treated from an elementary point of view; much new work on phosphorescence done by Prof. Urbain is described, and a few good plates of spectra are included. The German translation follows the French original very closely, the only alterations which have been made being the addition of some recent results and of some references to German literature.

OBITUARY.

DR. JULIUS LEWKOWITSCH.

WE much regret to have to report the death of Dr. Julius Lewkowitsch, which occurred on September 16th at Chamonix, after a short illness. Dr. Lewkowitsch was born in Prussian Silesia in 1857, and studied at Breslau under Prof. von Richter. After obtaining the degree of Doctor of Philosophy he remained at the University doing research work, in which his marked originality won for him great success. He afterwards became assistant to Dr. Landolt at the Berlin Agricultural High School, and subsequently assistant to Prof. Victor Meyer at Heidelberg. At this period Meyer was actively engaged in the investigation of problems in stereochemistry, and Lewkowitsch worked on the same subject, publishing many original papers. His life work, however, may be regarded as the development of the industries connected with Oils and Fats, and in the course of time he became the world's greatest authority upon the subject. He was the author of a standard treatise on "Oils, Fats, and Waxes" (London, 1898), which has been translated into English and German, and he also wrote "A Laboratory Companion to the Fats and Oils Industries" (London, 1901), and translated Benedikt-Ulzer's work "Analyse der Fette und Ole."

Dr. Lewkowitsch was a valued member of the Councils of the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry, which owed much to his administrative talents and his wide knowledge of technological problems.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 11, 1913.

New Decomposition of Oximes.—A. Angeli and Luigi Alessandri. — At 180° benzophenoxime undergoes rapid decomposition according to the equation $3C_{13}H_{11}NO = 3C_{13}H_{10}O + NH_3 + N_2$. The silver salt of the same compound decomposes at the ordinary temperature, regenerating benzophenone and liberating nitrogen. The yield of nitrogen obtained in one experiment was about 40 per cent of that calculated from the equation $C_{13}H_{10}NOAg = C_{13}H_{10}O + Ag + N$. Other oximes, *e.g.*, piperonal oxime, undergo the same reaction which is analogous to that of hydroxylamine :— $3NH_2OH = NH_3 + N_2 + 3H_2O$.

Thorium Molybdates.—A. Barbieri.—Neutral ammonium thorium molybdate, $(NH_4)_8Th(Mo_2O_7)_6.8H_2O$, can be obtained by adding a solution of anhydrous thorium sulphate to a solution of ammonium heptamolybdate and heating. The amorphous white precipitate first formed changes in appearance and becomes crystalline. The corresponding sodium salt can be prepared similarly. The acid salt, $(NH_4)_6H_2Th(Mo_2O_7)_6.11H_2O$, is prepared by adding to a nitric or hydrochloric solution of ammonium thorium molybdate a solution of ammonium nitrate, sulphate, or chloride. The solutions of alkaline thorium molybdates in dilute acids give the following reactions :— With salts of Ca, Rb, Cs, K, Sr, a white crystalline precipitate. With salts of Ba, Pb, Tl, Hg″, Hg′ a white amorphous precipitate. No precipitate with salts of magnesium or zinc. With salts of cadmium in concentrated solution a crystalline precipitate. With salts of aniline in concentrated solution a crystalline compound, which contains six atoms of nitrogen to one of thorium, and which is probably an acid thorium molybdate of aniline.

Compounds of Hydrated Salts with Organic Bases. —F. Calzolari.—The hydrated dithionates of Mg, Mn, Fe, Co, Ni form well-defined crystalline addition compounds with caffeine and hexamethylene tetramine, and with the latter the hydrated sulphates and thiosulphates of the same metals form similar compounds. The author has prepared and investigated a large number of these compounds, typical formulæ of which are :— $MgS_2O_6.8H_2O.2C_8H_{10}.N_4O_2$, $MgS_2O_6.6H_2O.2C_6N_4H_{12}$, $MgSO_4.9H_2O.C_6N_4H_{12}$, $MgS_2O_3.8H_2O.C_6N_4H_{12}$.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. Conversazione at King's College.

The Historical Medical Museum.—In response to numerous requests it has been decided to defer the closing of the Historical Medical Museum until October 31st. During the month of October it will remain open from 10 a.m. to 6 p.m. daily, and from 10 a.m. to 1 p.m. on Saturdays. After this date it will be closed for a few months for rearrangement as a permanent Museum. It is proposed to reopen the Museum in its permanent form in the spring of next year.

THE CHEMICAL NEWS.

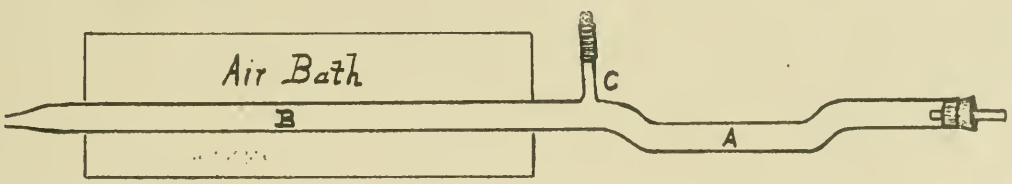
Vol. CVIII., No. 2812.

THE GLOW OF SULPHUR.

By W. H. WATSON.

Although not mentioned in the majority of text books, the fact that sulphur under certain circumstances exhibits a glow or "phosphorescence" has been frequently recorded. The method of obtaining the glow was described by Berzelius in his "Lehrbuch" (5th edition, vol. i., p. 185), and since then several investigators have turned their attention to the matter, but without arriving at an explanation of the phenomenon. The idea has been suggested that the glow was accompanied by the formation of a lower oxide of sulphur, possibly a monoxide, SO, but attempts to obtain such a body by Heumann (*Ber.*, xvi., 139), O. Jacobsen (*Ber.*. xvi., 478), and also by the writer, have proved unsuccessful. Experiments upon the oxidation of sulphur at low temperatures by Moissan (*Comptes Rendus*, 1903, xxxvii., 547) also lend no support to the idea. At the suggestion of Prof. H. B. Baker, to whom the writer desires to express his indebtedness, a further investigation of the phenomenon was undertaken with the results set forth below.

In the paper by Heumann referred to above, the author describes various methods of obtaining the glow, the most successful of which appears to be that of placing sulphur on a shallow tray supported above the bottom of an iron air-bath heated to about 240°, and allowing a current of air to pass over the molten sulphur. When the conditions are properly regulated, a large flame, differing in colour from the usual blue flame of burning sulphur and also in the fact that it is relatively cold (see also Baker, *Journ. Chem. Soc. Trans.*, 1900, lxxvii., 646), can be obtained and maintained for a considerable time. The author states that the slow combustion is accompanied by a curious smell which he compares to ozone or camphor.



These facts have been confirmed by the present writer, who found that the glow invariably exhibited itself as a curious luminous flicker over the heated base and adjacent parts of the sides of the oven, but never on the surface of the sulphur. Further experiments were made by means of an apparatus similar to that described below.

A piece of glass tubing, 40 to 50 cm. long and about 1 cm. bore, was bent as shown in the sketch, and had a narrow side-tube sealed in at C. Some pure re-crystallised sulphur, which had previously been kept melted for some time, was placed in the part A, while B was enclosed in an air-bath kept at 100—120° C. The sulphur was maintained at about 250°, while a slow current of pure dry air was passed through the apparatus, the side-tube C being closed. So long as the sulphur was kept below its ignition-point, no luminosity could be observed on the surface of the sulphur, but the air current became charged with a cloud of fine particles which were carried along the tube and not completely deposited before reaching the open end. In the portion of the tube within the air-bath, extending for some centimetres from the end nearer the melted sulphur, a steady glow could be observed, which, however, ceased if by any chance the liquid sulphur became ignited. The glow could be produced at any part of the tube B by heating gently at that part and allowing the rest to remain cool, even when B was of considerable length. By using a mixture of nitrogen and air a somewhat brighter glow was obtained, but the glow completely ceased if pure nitrogen were employed. In this latter case, however, it was possible to obtain a glow by introducing air through the side-tube C. It would therefore seem unlikely that the glow is connected with a preliminary action of oxygen on the heated sulphur.

If the air current after passing over the heated sulphur were filtered through a tube filled with recently ignited asbestos no glow whatever could be obtained in B, but the glow reappeared when the asbestos was removed. Similar results were obtained if cotton-wool or pieces of moist stick potash were used instead of asbestos. Bubbling the air through water was also effective, and a quantity of colloidal sulphur collected in the water.

In another series of experiments the gases escaping from the end of the tube in which the glow was taking place were led through a tube immersed in liquid air. A small amount of solid sulphur dioxide was collected, and in some cases a liquid. This latter, however, contained no sulphur compound other than a trace of sulphur dioxide, as on careful evaporation and bubbling the resulting gas through fuming nitric acid or a solution of potassium permanganate, no sulphuric acid was obtained. The gas contained about 40 per cent of free oxygen, and the residue appeared to be nitrogen and probably some argon. Similar results were obtained if the gases immediately after leaving the heated sulphur, and without allowing the glow to occur, were treated in the same way. In all cases the gas which escaped liquefaction by the liquid air was quite odourless.

There is therefore no direct evidence that an appreciable amount of an oxide of sulphur other than dioxide is formed at any stage. Heumann arrived at a similar conclusion from an analysis of the gases escaping from glowing sulphur. The glow appears to be caused by the oxidation of the particles of finely-divided sulphur resulting from the cooling of the air which has passed over the heated sulphur, and this view is in harmony with the observations recorded both here and in the records of earlier investigators. If this finely-divided sulphur is the result of some such reactions as the following — $2S+O_2=2SO$, then $2SO=SO_2+S$, the intermediate product must have a merely transient existence, and its presence would not be shown by chemical tests.

The finely-divided sulphur not only undergoes oxidation at a comparatively low temperature, but attacks copper and silver at the ordinary temperature with the production of black films of sulphide. Experiments made in order to discover whether the particles were electrified or not failed to show the existence of a charge. Air containing the finely-divided sulphur led through a tube containing an insulated piece of copper-foil connected with a delicate electroscope did not discharge the latter, whether the instrument carried a positive or negative charge. In other experiments the stream of finely-divided sulphur passed between two long strips of platinum foil, insulated and connected to opposite terminals of a small induction coil. Some 5 to 10 mgrms. of sulphur deposited on the plates in the course of an hour, but although the amounts deposited on the two plates were generally unequal, the variation

was not large, and, moreover, not constant. On the whole the results obtained were not decisive.

Summarising the results obtained, it may therefore be stated that when air passes over sulphur heated to a temperature below its ignition-point, the air becomes charged with sulphur vapour, which, as the temperature falls, separates as a mist or cloud of very small particles. The oxidation of this finely-divided sulphur gives rise to the phenomenon of the glow or "phosphorescence," but there is no evidence that at any stage any other oxide than sulphur dioxide is formed.

Imperial College of Science and Technology,
South Kensington, S.W.

SOME CURIOUS ATOMIC WEIGHT RELATIONS: QUATERNIAN SERIES.

By F. H. LORING.

Referring to my letter in the Chemical News (vol cviii., p. 95), may I call attention through your columns to a further extension of the quaternian series therein indicated.

It was shown that (1) argon, iron, bromine, and silver form a series in which the secondary differences in atomic weight stand in geometrical progression, these being 4 : 8 : 16 (argon taken twice), and their sum 28 (4×7). That (2) thallium, in some respects, resembles the alkali metals and silver, and appears to form the eligible end-member of a parallel series, namely, "9·75," cobalt, iodine, and thallium, the secondary atomic weight differences being 9·3 and 18·6, their sum 28 (4×7). It was shown that the differences approximate very closely to these values.*

It is now suggested that *helium*, *aluminium*, *manganese*, and *rubidium* form a similar series, in which the sum of the secondary differences may be taken as 7. The parallelism in certain chemical properties with the above elements of higher atomic weight is somewhat strained, yet upon a little study it will be seen that these elements seem singularly related to each other. Fresenius places aluminium and chromium together, and it is known that "aluminium is isomorphous with iron in the ferric state." (Tilden—"The Elements," 1910—points out this connection between aluminium and iron, and a periodic table is given in which iron is shown as a direct descendant from aluminium). Manganese appears to be heptavalent in Mn_2O_7, as is probably the case with chlorine in Cl_2O_7, whilst potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions, thus identifying this element with the halogens. Rubidium and thallium form some compounds which are isomorphous with each other. The relations are thus made apparent. The new series is as follows :—

	At. wts.	Differences.	
He	= 3·98		
		——23·15	
Al	= 27·13		——4·66 (*b*)
		——27·81	
Mn	= 54·94		——2·33 (*a*)
		——30·14	
Rb	= 85·08		

Experimental value, 85·45.

$2a = b$; $a+b = 7$.

The atomic weights employed throughout these studies are, for the most part, those harmonised by a scheme of elliptical curves (Chem. News, 1909, xcix., 148), rubidium being shifted so as to fall in the central part of the chart or tabular scheme to agree in position with its analogues, since the alkali metals form a group of elements more nearly alike than, perhaps, those of any other regular group of active members; if any irregularities in this respect exist this group should show it, although other groups do not in the system cited. This element so placed does not fall on a curve, but the positions of all the curves are not fixed. Such is my view, at any rate.

The value, 85·08, is slightly lower than the present accepted experimental figure, 85·45, but since rubidium appears to be radio-active in that it emits a feeble radiation (β-rays), it is possible that it may be contaminated with an appreciable amount of another element of higher atomic weight, which is radio-active. It is true that the absence of α-rays seems to preclude the possible presence of a well known radio-active element as an impurity, because the only known radio-elements of long period which emit β-rays give rise to, or are ultimately followed by, an α-ray product. No α-rays have been detected in the case of rubidium (see Rutherford, "Radio-active Substances and their Radiations," 1913, pp. 587—590).

Since the α-rays are rapidly ejected helium atoms, which belong to the even valency series (0—2—4—6), it is strange that some member of the odd valency series, such as hydrogen, is not likewise expelled, if only slowly, especially in connection with radio-elements belonging *properly* to the odd series (1—3—5—7), assuming that such radio-elements exist. Radium D, or actinium E (end-product), might have the value 210·43, which differs from the value "211·43" by exactly one whole unit, but it is not to be inferred that hydrogen atoms are emitted from the hypothetical impurity of rubidium, yet the idea has an experimental suggestion in it. The quoted value is of another series given below.

Attempts to allocate neon (20·00) at the head of a series have not been very successful. Nickel (58·66), though chemically beyond cobalt (59·00), is numerically below this element in position. Similarly, but in a reverse sense, tellurium (127·50) stands chemically before iodine (126·92), but numerically beyond this element.

The assumption that these chemically active elements are the nearest higher analogues, in one case in chemical position, and in the other in numerical place, leads to an extrapolated value, 211·43, which should be an analogue of silver or rubidium, or even thallium, and which by analogy might be an irregularly placed element in the Periodic Table. If I may offer a suggestion, such an element might be radio-active, and it might even be the impurity possibly present in rubidium.

It should be remembered that Sir J. J. Thomson has found an impurity in the purest neon thus far obtained, which fact, though not itself justifying the lower atomic weight above given, permits the use of the lower value with some reason, especially since this value is in harmony with many others adjusted by the system referred to above. The doubtful series is as follows :—

	At. wts.	Differences.	
Ne	= 20·00		
		——38·66	
Ni	= 58·66		——30·18 (*b*)
		——68·84	
Te	= 127·50		——15·09 (*a*)
		——83·93	
?	= 211·43		

(These elements appear to have closely associated neighbours:—"21·7," Co, I, "210·43 ?," and these are apparently the *regular* ones),

$2a = b$; $a+b = 45·27$.

The number of intervening active elements shows a fairly uniform progression, as is the case with the other elements singled out by this particular treatment (see Chemical News, cviii., 95).

There is one more series of doubtful character.

Mendeleeff predicted an inactive gas having an atomic weight of about half that of hydrogen (0·4). Several attempts to work out definite values have been made.

* The values employed were—107·9, 79·9, 55·9, 39·9, 39·9, 204·17, 126·92, 59·00, 9·75, 21·7 by further extrapolation, which may be J. J. Thomson's neon associate "22." (See last table).

The value 0·27 (see CHEMICAL NEWS, 1909, c., 281) is here tried as a head member of a quaternian series, but it is exceedingly doubtful whether this value is the right one, assuming the existence of such an element.

A series beginning with the above value in question can be arranged if *boron*, *magnesium*, and *potassium* be taken. On account of the radio-activity of the last-named element its *true* atomic weight, like that assumed in the case of rubidium, might be less than the present experimental value. The following table shows an attempt to bring into relation the atomic weights of these elements; this arrangement has some support from the regular progression of the intervening chemically active elements, nitrogen being taken as an inactive gas, which, in its diatomic state, it remembles :—

Intervening elements.	At. wts.	Differences.
	? = 0·27	
3		10·73
	B = 11·00	2·550 (*b*)
4		13·28
	Mg = 24·28	1·275 (*a*)
5		14·55
	K = 38·83	

Experimental value, 39·09.

(38·83 + 0·27 = 39·10, but this coincidence in values can hardly be regarded as significant).

$$2a = b\,;\ a+b = 3{\cdot}825.$$

Boron has properties which identify it with aluminium, bearing in mind that it is the first member of Group III., since initial or terminal members of a group usually show deviations from the characteristics common to members which comprise the major portion of the group.

Strong resemblances between Groups III., IV., and VIII., which may be regarded as being made up of branch members joining or forming part of the seventh group, are traceable through certain elements which exhibit characteristics common to these groups.

Magnesium certainly does not seem to be very closely related to manganese, but perhaps a careful comparative study of these two elements will reveal likenesses. Quoting from Senter's "Inorganic Chemistry" (1911, p. 527): -"*Manganese* and the halogens are the only known members of the seventh group. The former element, like those belonging to the sixth group just considered, forms compounds belonging to a variety of stages of oxidation, and shows analogies with *magnesium*, iron, chromium, and other elements, as well as the halogens." The italics are mine.

It is perhaps of interest to note that the decimal fractions of the values *a* and *b* are so related to the whole numbers that if the latter be represented as a_i and b_i, and the decimal fractions corresponding with these values be represented as a_f and b_f, then the equality of the ratios—

$$\frac{a_i}{a_f} = \frac{b_i}{b_f},$$

obtains in each case where fractions exist. This, of course, may be an accidental coincidence.

The following table shows the elements brought into special relation with each other by this method. In the table 0·27 = A', 21·7 = B', 9·75 = C', and 211·43 = D'.

	A'?		B		Mg		K	
	He		Al		Mn		Rb	
[Ar]		Ar		Fe		Br		Ag
[B']		C'?		Co		I		Tl
	Ne		Ni		Te		D'?	

This table appears to reconcile the value 21·7, and the duality of argon is made apparent, whatever this may mean. Has this peculiarity any connection with the probable fact that RaEm and AcEm are substantially or exactly the same in atomic weight?

These curious relations lead me to think that they are worth careful study, but whether they can be relied upon as devices for the adjustment of atomic weights, or as methods of extrapolation, is open to question. *Experiment only can determine this.*

Apart from the question of the ultimate utility of these methods, they do, in my opinion, point the way for certain lines of experiment, as, for example, the search for a radio-element in rubidium having chemical properties allied to thallium, or some element immediately beyond bismuth.

The elements gold, mercury, thallium, lead, and bismuth seem to embody some of the characteristics possessed by lower group members (these qualities being additional to other qualities which give them their higher place in the Periodic Table), as if, in some way, they, more than other elements, were the sweepings which included the fragments of materials intended for higher homologues of the lower groups.

CONNECTION BETWEEN BOILING-POINT AND MOLECULAR WEIGHT OF BODIES.

By J. C. THOMPSON.

III.

IT was shown (CHEMICAL NEWS, cvi., 178) that $\frac{T}{\sqrt{\rho}}$ is an approximate multiple of a constant, T representing the boiling-point of a liquid, ρ representing the density of its vapour.

This relationship, though holding fairly well for most inorganic bodies, for the more complex organic bodies gives figures differing widely from the constant. While attempting to extend the formula in order to include these organic bodies a remarkable relationship was discovered. This relationship is of extreme interest with regard to double bonds. The relationship becomes clear on evaluating—

$$\frac{T}{\rho_L^{0\cdot235}\,M^{0\cdot5}}$$

for hydrocarbons. $M^{0\cdot5}$ *the* $\sqrt{\text{molecular weight}}$ *has replaced* $\sqrt{\rho}$ as a more convenient number.

ρ_L is, as in Part II., the density of the body in the liquid state.

A rough correction is made in the final column to allow for the temperature at which the density is measured.

For every 1° C. of inaccuracy in boiling-point an average error of 0·1 in the factor results.

From these figures it is obvious that the greater the proportion of double and triple bonds in the molecule the greater the value of the function—

$$\frac{T}{\rho_L^{0\cdot235}\ {}^{0\cdot5}}.$$

Thus :—

(1)	Acetylene has its function of value ..	44·95
	Ethylene " " " ..	40·8
	Ethane " " " ..	40·4
(2)	Toluene gives	41·0
	Tetrahydrotoluene gives	40·1
	Hexahydrotoluene gives	39·5
(3)	Metaxylene gives	41·2
	Dihydro metaxylene gives	40·3
	Tetrahydro metaxylene gives	39·2
	Hexahydro metaxylene gives	39·2

That the formula—

$$\frac{T}{\rho_L^{0\cdot235}\,D^{0\cdot5}}$$

Formula.	Boiling-point, T.	Density, ρ_L.	Molecular weight, M.	$\frac{T}{\rho_L^{0\cdot235} M^{0\cdot5}}$.	$\frac{T}{\rho_L^{0\cdot235} M^{0\cdot5}}$ estimated for ρ at 0° C.
$H—C\equiv C\cdot H$ (acetylene)	190	0·45 at 0° C.	26	44·95	44·95
$CH:C.CH_2.CH_2.C:CH$ (dipropargyl)	358	0·81 ,, 20° C.	78	42·6	42·2
$C_6H_5C\equiv CH$	415	0·9295 ,, 20° C.	102	41·4	41·0
C_2H_4	170	0·361 ,, 0° C.	28	40·8	40·8
$C_6H_5CH=CH_2$	417	0·9074 ,, 20° C.	104	41·8	41·3
C_6H_6 (benzene)	353·5	0·874 ,, 20° C.	78	41·4	41·0
$C_6H_5CH_3$	383	0·869 ,, 16° C.	92	41·3	41·0
$C_6H_5C_2H_5$	407	0·876 ,, 10° C.	106	41·6	41·4
$C_6H_4(CH_3)_2$ (orthoxylene)	415	0·8932 ,, 0° C.	106	41·4	41·4
$C_6H_4(CH_3)_2$ (metaxylene)	412	0·8812 ,, 0° C.	106	41·2	41·2
$C_6H_4(CH_3)_2$ (paraxylene)	412	0·881 ,, 0° C.	106	41·2	41·2
$C_6H_3(CH_3)_3$ (mesitylene)	437·5	0·90 ,, 0° C.	120	41·0	41·0
$C_6H_4(C_2H_5)_2$ (meta)	455	0·8602 ,, 20° C.	134	40·7	40·2
$C_6H_6(CH_3)_2$ (orthodihydroxylene)	406	0·828 ,, 20° C.	108	40·8	40·3
$C_6H_6(CH_3)_2$ (metadihydroxylene)	392	0·814 ,, 20° C.	108	40·8	40·3
$(CH_3)_2C:CH_2$	267	0·637 ,, 14° C.	56	39·7	40·0
C_2H_6 (ethane)	183	0·446 ,, 0° C.	30	40·4	40·4
C_3H_8	235	0·536 ,, 0° C.	44	41·0	41·0
C_4H_{10}	274	0·600 ,, 9° C.	58	40·6	40·6
C_5H_{12} (normal)	309	0·633 ,, 15° C.	72	40·6	40·3
C_5H_{12} (iso)	301	0·627 ,, 15° C.	72	39·6	39·3
C_7H_{16}	371	0·700 ,, 0° C.	100	40·3	40·3
$C_{10}H_{22}$	446	0·745 ,, 0° C.	142	40·1	40·1
$C_6H_9CH_3$ (tetrahydrotoluene)	377	0·797 ,, 18° C.	96	40·6	40·1
$C_6H_8(CH_3)_2$ (metatetrahydroxylene)	392	0·794 ,, 14° C. 0·814 ,, 0° C.	110	39·5 39·2	39·2
C_6H_{12} (hexahydrobenzene)	343	0·7473 ,, 0° C.	84	40·1	40·1
C_7H_{14} (hexahydrotoluene)	368	0·7723 ,, 0° C.	98	39·5	39·5
C_8H_{16} (hexahydrometaxylene)	391	0·781 ,, 0° C.	112	39·2	39·2
C_8H_{16} (para)	410·6	0·7956 ,, 4° C.	112	40·9	40·8
$C_3H_7C_6H_{11}$	421	0·787 ,, 20° C.	126	39·7	39·2
$CH_3C_6H_{10}C_3H_7$	445	0·8116 ,, 17° C.	140	39·5	39·1

is the completely correct form is highly improbable as it is not deduced from theoretical considerations. But that boiling point, density as liquid, molecular weight, and degree of saturation are nearly related in this manner can be readily seen.

IV.

A theory which can explain the influence of double bonds will now be put forward. The carbon atom is supposed to possess four valencies placed so that if the carbon atom be at the centre of a tetrahedron each valency is in the direction of one of the corners. Now these valencies are treated by Baeyer in his tension theory as though of a semi-rigid nature capable of bending when subjected to strain. It appears, however, far better to consider these valencies as possessing the properties of forces of attraction. A double linkage becoming the resultant of two of these forces. A triple linkage becoming the resultant of three of these forces.

Now with four equal forces placed in this manner the resultant of two or three of them is obtained by mathematics. Thus if each force be considered equal to f, the resultant of two of them $= \frac{2}{3}\sqrt{3}f = 1\cdot155$, the resultant of three of them $= f$.

Consider now the three bodies :—(1) Ethane, (2) ethylene, and (3) acetylene.

The forces connecting their carbon atoms together are, in the first case, for each carbon atom f, in the second case $1\cdot155\,f$, in the third case f. In the second and the third a portion of the valency forces possessed by the carbon atoms has not been used, for a normal carbon atom should possess forces amounting in value to $4f$. In the second case the force value $= 3\cdot155\,f$. In the third case the force value $= 2f$.

Thus in the second case there is for each carbon atom a force of $0\cdot845\,f$, and in the third of $2f$ not used within the molecule. By "being used within the molecule" is meant neutralised by other forces within the molecule. Now, any forces of attraction not used within the molecule, owing to there being no matter within the molecule to act upon, will be used in attracting neighbouring matter. The normal saturated molecule attracts neighbouring molecules, and is kept from neighbouring molecules by its kinetic energy. The unsaturated molecule will be attracted with a greater force than the saturated.

It has been shown (see Part II.) that $\frac{\rho_L T}{m}$ varies as A, where A is the attractive pressure exerted at the boiling-point of the liquid.

Now, from the kinetic theory ρ_L varies directly as the pressure ; temperature remaining constant. Similarly, temperature varies directly as the pressure ; density remaining constant. That is to say, that an increase in pressure will have the same effect upon the density as it has upon the temperature.

Now, in the expression—

$$\frac{T}{\rho_L^{0\cdot235} M^{0\cdot5}}$$

it is required to find the effect of an increased attractive force. Owing to the nature of the force producing the increase in attraction it will be independent of the molecular weight. Also, since T for increase of attraction varies in the same manner as ρ_L, the expression—

$$\frac{\rho_L}{\rho_L^{0\cdot235}}$$

will vary in the same way as—

$$\frac{T}{\rho_L^{0\cdot235} M^{0\cdot5}}$$

with respect to attractive pressure. But—

$$\frac{\rho_L}{\rho_L^{0\cdot235}} = \rho_L^{0\cdot765}.$$

Since ρ_L increases with pressure, $\rho_L^{0.765}$ increases with pressure; that is, the expression—

$$\frac{T}{\rho_L^{0.235} M^{0.5}}$$

increases in value when there is an increase in the attractive forces of the molecule, or the forces due to the unsaturation of the molecule increase the value of the expression—

$$\frac{T}{\rho_L^{0.235} M^{0.5}}.$$

NOTE ON CHEMICAL NOMENCLATURE.

By GERALD HARGRAVE MARTIN.

Chemists call the compound HgS mercuric sulphide or sulphide of mercury, but they never refer to it as sulphur mercuride. At first sight the reason for this custom is not obvious. When two elements combine they disappear, and a new substance with different properties appears in their place. Empedocles attributed the properties of substances to his metaphysical elements, or principles, which were carried by one original matter; and under Aristotle's care this view became widely accepted.

While this view prevailed there was no reason why the names of the disappearing substances should be included in the name given to the substance which appears in their place. Thus, when Geber prepared mercury sulphide artificially, he called it usifur.

During the middle ages the metaphysical elements became replaced by material elements; thus the metaphysical sulphur and mercury of Geber became materialised into brimstone and quicksilver, and during the iatro-chemical period it became realised that cinnabar was composed of these two substances. After the chemical revolution the balance reigned supreme in chemistry, and the properties of compounds were attributed to their ponderable composition. The elements were generally supposed to continue to exist in their compounds, although in a disguised form.

In what order should the names of the elements appear in those of their compounds? The modern chemist has no logical reason for regarding either element in a binary compound as being of greater importance than the other. To the alchemist, however, the metals were by far the most important substances; thus there were noble metals resembling that most noble and perfect metal gold; there were base metals; there were bastard metals; and, lastly, there were non-metallic substances. Beside their monetary value the metals have played a most important *rôle* during our civilisation. Thus the stone ages were followed by the bronze age, and we are still living in the iron age.

Now it is the miserable non-metallic elements which combine most readily with the metals, so who could hesitate as to which element should have the place of honour in the name of the compound? You might say sulphuret or sulphide of mercury, or mercury sulphide, but it was not meet to say mercuride of sulphur, or sulphur mercuride.

Hence the name of the metal occupied the place of honour in the name of the compound, for were not the metals the most important things in inorganic nature? The chemists inherited this custom of honouring the metals from the alchemists; the terms noble and base metal have survived. Mercury sulphide is described in the text-books under the compounds of mercury, and not under the compounds of sulphur; its formula is written HgS and not SHg. In compounds which contain no metal the more positive element or radical, which apes a metal in the compound, was presumably from force of custom given the place of honour. Thus, water was hydrogen monoxide, or oxide of hydrogen, but was never called oxygen hydride; CS_2 was carbon bisulphide, not sulphur carbide.

Although, after Lavoisier's chemical revolution, oxygen played a most important *rôle* in chemical theory it could not have the place of honour in the names of its compounds, for it was the least metal-like or most electronegative element known. Thus, although chemists wrote of chloride of nitrogen, and not of nitride of chlorine, the compounds Cl_2O, ClO_2, &c., were called oxides of chlorine, and not chlorides of oxygen. This custom has also been generally observed in organic chemistry; CH_3I is called methyl iodide, not iodine methyl. Although in the compound $C_2H_5—S—C_2H_5$ the sulphur is regarded as binding the two ethyl groups together, the compound is always called ethyl sulphide, never sulphur ethide.

The positive radicals, however, had to cede the place of honour to a genuine metal; thus, although $(C_2H_5)_2S$ was ethyl sulphide, $(C_2H_5)_2Zn$ was zinc ethyl, but not ethyl zincide. We find the rule observed even in the Grignard compounds such as magnesium methyl-iodide, although the names magneside of methyl iodide, or iodine methyl magneside, would be just as logical.

22, Milestone Road, Upper Norwood, S.E.

NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

If two solid crystals of the same substance in different orientation are brought into contact with one another, they remain unaltered. On the other band, two liquid crystals flow together and endeavour to assume the same structure as is shown by the alteration of the orientation of the optical anisotropism. Thus the molecules of the liquid crystals are mobile, but their arrangement is not quite irregular as in ordinary liquids; they exert a directive force upon one another, like magnets which are free to move, or rather like astatic magnetic systems (see O. Lehmann, "Die neue Welt der flüssigen Kristalle," 1911, 346).

This mobile state of equilibrium remains unchanged as long as the external conditions which influence it are unaltered. After any disturbance which is not too deep-seated it returns to its original condition when the external conditions again become the same. Only in rare cases does the arrangement of the molecules correspond to the grating structure of ordinary solid crystals. Usually only the axis about which the molecules easily turn is parallel for all molecules, while the secondary axes, perpendicular to it, take up all possible positions, which continually alter. This semi- or pseudoisotropic structure (*loc. cit.*, p. 196 *et seq.*) is midway between that of homogeneous solid crystals and that of homogeneous non crystalline liquids. Very frequently, however, the structure is not even homogeneous; discontinuity of structure, the formation of twins, sphaerolithic and fan-like groupings of the chief axes of the molecules, conical disturbances, &c., occur, as has already been mentioned in earlier researches.

The essential properties of crystalline liquid substances, like melting, solidification, and transition points, solubility, vapour tension, &c., are unaffected by these modifications of the molecular arrangement; thus there is no transition to another "phase." Alterations of anisotropism cannot be explained on the hypothesis that matter is continuous, and thus they are proofs of the existence of molecules.

But even on the basis of existing molecular theories the possibility of such mobile equilibria of the molecules cannot be deduced. They constitute a perfectly new physical fact, which, if it can be satisfactorily explained, must necessarily lead to important results as regards molecular forces. But even if the explanation is not forthcoming this new fact is of importance, inasmuch as it considerably

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

limits the number of possible molecular hypotheses. Accurate empirical investigation of the facts is obviously what is now required in this region.

The flowing together of two crystals to form a single crystal was observed for the first time in the modification of ammonium oleate called "Schmierseife" (*Zeit. Phys. Chem.*, 1895, xviii., 91; "Die neue Welt der flüssigen Kristalle," p. 175). On account of some objections which have been put forward (see A. Mlodziejowski, *Zeit. f. Kristallogr.*, 1913, lii., 1) I have extended these observations.

I.—*The Preparation of Liquid-crystalline Ammonium Oleate.*

Herr Mlodziejowski recommends the following method (*loc. cit.*, p. 1):—"The oleic acid was mixed with much aqueous ammonia in a test-tube, the liquid was poured off the precipitate, and the latter was dissolved in ethyl alcohol." Now it is not impossible to obtain thus a preparation which forms liquid crystals, but it is not the same as those investigated by me, as I shall presently show, and usually no result is obtained. For if much ammonia is really used no precipitate with a superincumbent liquid results, but only a turbid colloidal solution (soap water) from which no precipitate settles even after it has stood for some time. In any case, the method is faulty because a preparation which is too rich in water is obtained. If preparations are used which are evaporating freely as Herr Mlodziejowski recommends, and from which the alcohol is escaping more rapidly than the water, the error is still greater. No excess of water must be present, *i.e.*, the proportions of water and ammonia must be correctly chosen. This is impossible if the oleic acid is treated with commercial ammonia.

As I have previously stated, to obtain the preparation it is best to pass ammonia gas from a steel cylinder into oleic acid till it smells strongly of ammonia (Note 1). Thus a neutral anhydrous oleate ammonium is obtained. If this is fused under a cover-glass on a slide (care being taken that no bubbles arise owing to decomposition), and the cooling is watched under a microscope, it is seen that the mass solidifies as a whole to small needle-shaped (rhombic?) crystals of a labile modification. These are soon converted into a rather less fusible stable modification appearing as imperfectly formed (monoclinic?) leaflets. From alcoholic solution these latter can be obtained as relatively large crystals with sharp edges. If the crystalline mass is rubbed up with a trace of water, without the addition of alcohol (Note 2), and after previously warming it, the process of crystallisation is watched, it is observed that this is not a single process as before; it is seen that liquid crystals first separate, and after some time these are absorbed by the small needle-like crystals or the stable leaflets. The process can be followed still better in presence of alcohol. If the concentration is not uniform the leaflets crystallise out after some time in the regions of greater concentration. These regions are bordered by a zone filled with labile needles and appearing less light (grey) through crossed Nicols. Outside this second zone there is a third zone of liquid crystals which by flowing together may form individuals of considerable size. The limits of the zones gradually spread outwards, and after waiting a little it will be seen that the whole has been transformed into the leaflet modification (Note 3). The greater the amount of water added the more the quantity of liquid crystals increases at the expense of the solid, but the tendency to change into the latter is smaller.

Herr Mlodziejowski (*loc. cit.*, p. 3) disputes the correctness of my statement that the liquid crystals are absorbed by the solid crystals. The discrepancy is easily explained, for Herr M. did not employ my method for preparing the substance, but a simpler method, as described above, in which he did not obtain the anhydrous solid crystals of neutral ammonium oleate observed by me. Thus he was working with another substance.

Taking into account the fact that he speaks of a precipitate from which the superincumbent liquid was poured off, and which consisted of drops of oleic acid with a stiff crust of soap, it may be assumed that his preparations contained not only water but also oleic acid in excess, so that the solid crystals observed by him were crystals of acid ammonium oleate hydrate. These naturally do not absorb the liquid crystals of neutral ammonium oleate hydrate, for they are not polymorphic modifications of the latter.

An anhydrous acid ammonium oleate does not exist. Solid neutral ammonium oleate certainly dissolves in oleic acid (as in alcohol), but it crystallises out again unchanged. If some water is added the different shaped much larger crystals of the acid hydrate separate from the solution; they can also be obtained by rubbing up the liquid-crystalline ammonium oleate hydrate with a sufficient quantity of oleic acid (by means of a spatulum on a sheet of glass). The oleic acid completely disappears if the right amount is used, and the mass which was previously liquid-syrupy becomes wax-like and solid. If oleic acid is present in excess, or if some alcohol is added as solvent, the substance is covered with a cover-glass shaped like a clock-glass, warmed, and then allowed to cool, crystals of this acid hydrate of ammonium oleate can be obtained. They possess remarkable shapes owing to the frequent occurrence of fan-shaped structural disturbances (see the photographs in the author's book "Flüssige Kristalle," 1904, Table I., Figs. 1—3 and Figs. 4—6, and Table II., Figs. 1—3, 5; the substance is not an absorption compound of neutral oleate with oleic acid, or a solid solution in the former, as was previously stated). If the quantities of oleic acid and water were originally insufficient they may be obtained in addition to the solid anhydrous crystals of the neutral ammonium oleate. A mutual disturbance naturally does not occur any more than in presence of liquid crystals. As was to be expected the liquid crystals can be obtained from them by the addition of ammonia.

We shall now return to the original experiments. If we continue to add water to the solid anhydrous crystals of ammonium oleate it may easily be seen under the microscope that when the amount of water has reached a certain definite limit the whole mass is converted into the syrupy liquid-crystalline modification. Thenceforward no needles or leaflets of the anhydrous modification appear; the mass has become neutral ammonium oleate hydrate. The chemical change can easily be followed macroscopically if some of the anhydrous mass is mixed by means of a small spatulum on a glass plate with more and more water. The water completely disappears, and finally the mass becomes uniform and is now no longer solid and waxy as originally, but liquid and syrupy. At the moment at which the last traces of leaflets disappear we have the pure liquid crystalline modification.

The same observation can be made with a solution of the anhydrous modification in alcohol. In this case also the continued addition of small quantities of water causes the appearance of liquid crystals, and after the addition of the right quantity only the latter crystallise out. Instead of pure water it is better in all cases to use water saturated with ammonia, as the ammonia present cannot do any harm, and may prevent the hydrolytic decomposition of the ammonium oleate (Note 4).

The fact that the hydrated liquid-crystalline modification crystallises out unchanged from anhydrous alcohol is a proof that the water is not water of crystallisation but firmly combined hydrate water, for absolute alcohol usually absorbs the water of crystallisation from salts containing it.

This stability of liquid crystals towards alcohol and other solvents makes it possible to purify them by recrystallisation like solid crystals. For instance, the ammonium oleate is rubbed up in a porcelain dish, kept warm by means of a water-bath, until a clear solution is obtained, and then this is poured into a closed separating funnel, and allowed to cool. After some time the solution becomes turbid owing to the separation of isolated small crystals. These gradually sink to the bottom, and form a

thick deposit just like a turbid but translucent deposit, consisting of solid crystals which separates from other solutions. The liquid-crystalline layer can then be separated by pouring off the mother-liquor, but it is not possible to effect complete separation because the crystals are always mixed with some alcohol.

Notes.

1. (*Ann. d. Phys.*, 1906, xxxi., 183. The chemical factory of E. Merck, Darmstadt, supplies a preparation specially for the demonstration of liquid crystals at 5.10 Mk. for 100 grms.; the raw oleate at 1.65 Mk. for 1 kgrm. can also be used. If a solution is required in order to prevent the mass getting stiff, which makes it difficult to pass the ammonia through, alcohol is added to the oleic acid; this partly dissolves the oleate so that a fairly liquid paste is obtained.

2. It is sufficient to leave the preparation uncovered for some time, when it absorbs moisture from the air, or to breathe on it.

3. For this reason I have previously suggested that the liquid crystals may be a labile modification of ammonium oleate which could be preserved by the addition of suitable substances. Closer investigation has shown that this suggestion is not correct. The chief effect of the addition of any substance is produced by the water it contains. Thus if anhydrous ammonium oleate and the syrupy liquid crystalline modification are brought together on a slide under a cover-glass and warmed till fusion occurs, the leaflets which form on cooling do spread somewhat into the liquid-crystalline (partly semi-isotropic) mass, but only as far as the latter contains anhydrous oleate mixed with it or dissolved. Possibly the liquid crystals separating in such mixtures can be regarded as mixed crystals with the anhydrous oleate, which is also suggested by the fact that they show only a very slight tendency to flow together.

4. According to Kraft and Stern, *Ber.*, 1894, xxvii., 1755, no basic oleic acid salts are formed.

(To be continued).

ON THE

PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS.*

By LeRoy McMaster.

(Concluded from p. 183).

Ammonium m-*Phthalate.*—On passing ammonia gas into an alcoholic solution of *m*-phthalic acid a very voluminous white gelatinous precipitate was formed, which changed to a white powder. The salt was filtered by suction, and washed with only a small amount of alcohol, as it is somewhat soluble in this medium in the absence of the ammonia. The complete precipitation of this salt in alcohol depends, therefore, upon an excess of ammonia. Ammonium *o*-phthalate, on the other hand, is quite insoluble in alcohol. It was impossible to prepare ammonium *p*-phthalate by this method on account of the insolubility of *p*-phthalic acid in both alcohol and ether.

The ammonium *m*-phthalate was dried in a desiccator, and, on analysis, gave :—

N calculated for $C_6H_4(CO_2NH_4)_2$ . ..	14·00
Found	13·96

The method having proved so very applicable in the preparation of neutral ammonium salts of dibasic acids, it was next tried on the preparation of neutral ammonium salts of monobasic acids. Some work is in progress in the Washington University on the preparation of neutral salts of tribasic acids by the same method.

* Presented before the St. Louis Academy of Science, February 17, 1913. From the *American Chemical Journal*, xlix., No. 4.

Ammonium Propionate.—When ammonia gas was first passed into an ethereal solution of propionic acid, no precipitate formed. White fumes came off which condensed in the top of the flask to a beautiful snow-white substance. After the gas was passed in for a short time, a white voluminous precipitate formed. The precipitate was quickly filtered by suction, washed with ether, placed in a vacuum desiccator for a few minutes, and then in a calcium chloride desiccator. The salt deliquesces very readily, and is very soluble in water. On first dissolving the salt in water, the solution is neutral. The solution, however, soon turns acid, due to hydrolysis. The salt is very soluble in methyl alcohol, ethyl alcohol, and acetic acid. Analysis proved it to be the neutral ammonium propionate.

N calculated for $C_2H_5CO_2NH_4$	15·38
Found	15·4

Ammonium Isobutyrate.—Isobutyric acid was dissolved in ether, and ammonia passed into the solution. A snow-white precipitate of lustrous appearance formed. This was filtered by suction, washed with ether, and dried in a desiccator. Though not deliquescent, the salt cannot be dried in the air, for it has a very high vapour tension. An appreciable quantity of the salt will disappear entirely in a short time if exposed to the air. The salt is soluble in alcohol and water. The aqueous solution is neutral. Determination of nitrogen by the Kjeldahl method gave :—

N calculated for $C_4H_7O_2NH_4$	13·33
Found	13·32

Ammonium Benzoate.—By evaporating a solution of benzoic acid neutralised with ammonia there is obtained an acid salt of the formula $NH_4C_7H_5O_2.C_7H_6O_2$ (Berzelius). The neutral salt can be obtained by conducting ammonia gas into an ethereal solution of benzoic acid. A white gelatinous precipitate was formed, which, after being filtered and washed with ether, dried in the air to an amorphous powder. It is not deliquescent, but soluble in water, in which it shows a neutral reaction. The salt is somewhat soluble in ethyl alcohol, from which it can be crystallised. Analysis proved it to be the neutral ammonium benzoate.

N calculated for $C_6H_5CO_6NH_4$	11·02
Found	11·02

Ammonium Cinnamate.—When ammonia gas was passed into an ethereal solution of cinnamic acid a white gelatinous precipitate at first formed which turned to an amorphous powder. It was necessary to pass the gas into the solution for several hours in order to obtain the neutral salt. The salt is soluble in water and is not deliquescent in the air. If the salt is crystallised from alcohol, beautiful white crystals are formed which have a marked odour of oil of cinnamon. The original salt prepared in ether has no such odour. Also, the salt crystallised from alcohol is very much less soluble in water than the original salt. Ammonia was passed into an alcoholic solution of cinnamic acid, and there were formed at once glistening white crystals. After the ammonia was passed into the solution for some time, the alcohol was poured off from the crystals into a crystallising dish, and allowed to evaporate spontaneously. A further quantity of the crystals was obtained. These crystals, prepared from the alcoholic solution of the acid, had an odour of oil of cinnamon, but not so marked as in the case of the salt prepared in ethereal solution and afterwards crystallised from alcohol. The crystals prepared in alcohol were again found to be much less soluble in water than the amorphous powder prepared in ether. Determination of nitrogen in the salt prepared in ether gave the result :—

N calculated for $C_9H_7O_2NH_4$	8·48
Found	8·49

Action of Ammonia on Palmitic Acid.—When dry ammonia gas was passed into an ethereal solution of palmitic acid there was produced at once a very voluminous

white gelatinous precipitate. The precipitate did not become crystalline even after passing in the gas for three hours. The precipitate was filtered by suction and washed with ether. It dried in the air to a white substance resembling a "soap." It was soluble in alcohol, especially if the alcohol was warm. Ammonia was also passed into an alcoholic solution of palmitic acid for three hours. No precipitate formed at first, but as the ammonia gas continued to pass into the solution a precipitate was formed which after a while dissolved, and again after a short time re-precipitated. The precipitate and alcoholic solution were poured into a crystallising dish and the alcohol allowed to evaporate. While wet with alcohol the precipitate was granular in appearance, but after the alcohol had entirely evaporated and the compound became dry, it had the appearance of the compound prepared in ether. The compound prepared in each case was evidently an ammonium "soap." It was not analysed.

This investigation is being continued with other organic acids.

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

(Continued from p. 182).

PART II.—*Analysis of the Group:* (a) *General Discussion;* (b) *Test Experiments;* (c) *Adopted Procedure; Notes.*

(a) *General Discussion.*—In nearly all the schemes of qualitative analysis known to the authors the group precipitate is treated first with dilute hydrochloric acid in the effort to separate the readily soluble zinc and manganese sulphides from the more difficultly soluble sulphides of nickel and cobalt. Although this method is in very general use, the experiments conducted in this laboratory indicate that it does not meet the requirements of an accurate system of qualitative analysis. That others have experienced difficulties in endeavouring to make the separation is evidenced by the fact that the strength of the hydrochloric acid to be used in making the separation, as recommended by various authors, ranges from 0·5N to 5N. (Dennis and Whittlesey recommend 1N HCl; W. C. Morgan recommends 1N HCl; J. Stieglitz recommends 1N HCl (approx.); A. A. Noyes recommends 2N HCl; O. F. Tower recommends 2N HCl; J. H. Long recommends 2N HCl; F. M. Perkin recommends 2N HCl; F. P. Treadwell recommends 2·5N HCl; W. Böttger recommends 0·5N HCl; W. Segerblom recommends 5N HCl. Gooch and Walker separate Mn from Zn, Co, and Ni by the use of $HC_2H_3O_2$.) Our experiments, as well as those of others (Hertz, *Zeit. Anorg. Chem.*), 1901, xxvii., 390; 1901, xxviii., 343), have shown that the sulphides of nickel and cobalt are moderately soluble in 1N HCl, and that the presence of nickel and cobalt in the filtrate seriously interferes with the tests for zinc and manganese; if a weaker acid is used then the zinc frequently escapes detection by remaining in the residue, for it is known that zinc sulphide in the presence of nickel or manganese sulphide is not readily soluble in 0·1N HCl. Again, there is evidence at hand which indicates that the rate at which different sulphides dissolve in an acid of given strength is variable, and depends apparently upon the state of aggregation. In view of these difficulties, this method has been abandoned, and instead, all the sulphides are brought into solution by the use of hydrochloric acid and (solid) potassium chlorate.

The next step in the proposed method of analysis is the separation of zinc from manganese, nickel, and cobalt by the addition of sodium hydroxide and sodium peroxide. One of the main problems of this investigation was the determination of conditions which would insure an accurate separation of zinc. It is believed that the method as worked out and described in this paper has not been applied by any other author. By the treatment just mentioned, the manganese, nickel, and cobalt are completely precipitated as hydroxides of these metals in the trivalent condition and the zinc remains in the solution as sodium zincate. In this separation, advantage is taken of the fact which seems to have been overlooked by the majority of authors, namely, that cobaltic hydroxide, $Co(OH)_3$, is much less soluble than cobaltous hydroxide, $Co(OH)_2$, in an excess of sodium hydroxide. The zinc is precipitated and confirmed by conventional processes.

The separation of the hydroxides of manganese, nickel, and cobalt presented one of the most difficult problems connected with this investigation. The reaction finally selected for the purpose of separating manganese from nickel and cobalt is known as "Ford's Reaction." This reaction is frequently employed in iron and steel analysis, and consists in the conversion of the manganese into manganese dioxide by the action of chloric acid in the presence of strong nitric acid. The method of separating the manganese consists in dissolving the three hydroxides in strong hydrochloric acid, evaporating to a small bulk with an excess of nitric acid (1·20), adding (solid) potassium chlorate, boiling, and finally filtering off the manganese dioxide on a glass-wool-asbestos filter. This method has an advantage over the usual colour tests for manganese, in that an idea of the quantity of the element present may be obtained. Although a confirmatory test is unnecessary, the usual colour tests have been worked out and fitted to the system. Objections may be offered to this method, as it involves the use of an asbestos filter. When the operation (see Procedure IV., Note 2) has been executed once the objections will, in all probability, be withdrawn.

The filtrate (from the chloric acid precipitate) containing the nickel and cobalt is evaporated to expel the excess of acid and then made neutral with sodium hydroxide. The solution is divided into two parts and a test is made for each metal in the presence of the other; the nickel is precipitated by the use of potassium cyanide, sodium hydroxide, and bromine water as nickelic hydroxide; and the cobalt as potassium cobaltic nitrite by the use of acetic acid and potassium nitrite. Provision is made for the usual borax-bead tests.

(b) *Test Experiments and References.* Series III.—Solubility of the Sulphides of Zinc, Manganese, Nickel, and Cobalt in Hydrochloric Acid.

0·2 grm. of Mn and 0·2 grm. of Zn as sulphides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1N HCl; after 5 minutes treatment the sulphides were completely dissolved.

0·2 grm. of Ni and 0·2 grm. of Co as sulphides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1N HCl; after 10 minutes treatment the mixture was filtered and the filtrate tested for Ni and Co by adding NH_4OH and H_2S. A heavy black precipitate appeared at once. Approximately 0·04 grm. of Ni and Co had dissolved.

This series of experiments shows that sulphides of nickel and cobalt are moderately soluble in 1N HCl. Therefore zinc and manganese cannot be completely separated from nickel and cobalt by the use of this reagent.

Series IV.—Action of Hydrochloric Acid on Various Mixtures of the Sulphides of the Group.

0·2 grm. of Ni and 0·0005 grm. of Zn as sulphides were treated with 25 cc. of 1N HCl; after ten minutes treatment the mixture was filtered and the filtrate tested for Zn by adding NH_4OH and H_2S. A heavy, black precipitate appeared at once, indicating that the NiS had dissolved. The *white* sulphide of zinc escaped detection, owing to the presence of a large mass of *black* nickel sulphide. Similar results were obtained when the experiment was

* *Journal of the American Chemical Society*, xxxv., No. 5.

repeated with quantities of Zn as ZnS varying in amount from 0·001 grm. to 0·02 grm.

These experiments show that a quantity of Zn as large as 0·02 grm. escaped detection, owing to the presence the Ni dissolved by the 1N HCl.

0·2 grm. of Zn and 0·0002 grm. of Ni as sulphides were treated with 25 cc. of 1N HCl; after 10 minutes treatment the sulphides were completely dissolved. This experiment was repeated with quantities of Ni varying in amount from 0·0003 grm. to 0·001 grm. Quantities of Ni smaller than than 0·0005 grm. were completely dissolved; on the other hand, it was found that ZnS in the presence of NiS was not completely dissolved in 1N HCl. Owing to these facts small amounts of Zn in the presence of relatively large amounts of Ni escaped detection.

Series V.—Action of Hydrochloric Acid and Potassium Chlorate on Mixtures of Sulphides.

0·2 grm. of Mn, 0·2 grm. of Zn, 0·2 grm. of Ni, and 0·2 grm. of Co as sulphides were treated with 25 cc. of HCl (1 : 12), and the mixture boiled for 5 minutes. A black residue proved to be a mixture of NiS and CoS. A few crystals of $KClO_3$ were added to the mixture. The residue dissolved at once.

Series VI.—Behaviour of Sodium Hydroxide and Sodium Peroxide towards Zinc, Manganese, and Nickel Hydroxides.

A solution containing 0·3 grm. of Zn as $ZnCl_2$ was made slightly alkaline with 5N NaOH. A white precipitate of $Zn(OH)_2$ appeared at once. The mixture was divided into two equal portions. When NaOH was added in moderate excess to one portion the $Zn(OH)_2$ dissolved, forming a clear solution of sodium zincate. A few grains of Na_2O_2 were added to the other portion—the $Zn(OH)_2$ was readily dissolved.

Similar results were obtained when the above experiments were repeated with hot solutions.

The composition of sodium zincate is probably not definitely known. Kunchert (*Zeit. Anorg. Chem.*, 1904, xli., 343—348) using Bodländer's electromotive-force method proved that solutions of sodium zincate contain chiefly ZnO_2^{--} and some $HZnO_2^-$. Forster (*Zeit. Elecktrochem.*, 1899, vi., 301) has prepared solid $NaHZnO_2$. Hantzsch (*Zeit. Anorg. Chem.*, 1902, xxx., 298—303) from conductivity measurements, and Fisher and Hertz (*Zeit. Anorg. Chem.*, 1902, xxxi., 355) from dialysis experiments concluded that sodium zincate is almost completely hydrolysed into NaOH and $Zn(OH)_2$, and that the latter is present as a colloid.

0·2 grm. of Mn as $MnCl_2$ was completely precipitated by NaOH as flesh-coloured $Mn(OH)_2$, which turned brown owing to its oxidation (in the presence of air) to $MnO(OH)_2$. $Mn(OH)_2$ was found to be insoluble in excess of NaOH. $Mn(OH)_2$ is converted by Na_2O_2 into the brown hydrated MnO_2, probably $MnO(OH)_2$. The precipitation of Mn as $MnO(OH)_2$ by the use of NaOH and Na_2O_2 was complete.

From a solution containing 0·03 grm. of Ni as $NiCl_2$, NaOH, when added to alkaline reaction, completely precipitated the Ni as $Ni(OH)_2$. The precipitate was insoluble in excess of the precipitant. The precipitate was converted into black $Ni(OH)_3$ when treated with Na_2O_2. The filtrate gave negative results when tested for Ni.

Series VII.—Behaviour of Cobalt Salts towards Sodium Hydroxide and Sodium Peroxide.

0·03 grm. of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made just alkaline with 5N NaOH, then 10 cc. *excess* were added and the mixture heated to boiling. The precipitate was filtered off, and the blue-coloured solution was acidified, then made just alkaline, and saturated with H_2S. A precipitate of CoS separated. This experiment was repeated, but 4 grms. of Na_2O_2 was added *before* the mixture was heated to boiling. The precipitate was converted into black $Co(OH)_3$, which was removed by filtration. The filtrate possessed a blue colour, which indicated that some of the cobalt had dissolved in the alkaline solution, forming a soluble salt, probably Na_2CoO_2, and when tested, as in the previous experiment, CoS separated.

0·03 grm. of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made *slightly* alkaline with 5N NaOH. *No excess* of this reagent was added. 0·4 grm. of Na_2O_2 was added and the mixture heated to boiling. The dark coloured precipitate of $Co(OH)_3$ was filtered off; the filtrate was colourless and yielded no test for Co. This experiment was repeated many times with quantities of Co varying in amount from 0·0003 grm. to 0·5 grm.; in each experiment the precipitation was complete, the filtrate being colourless.

This series of experiments indicate that cobalt*ous* salts dissolve in excess of NaOH forming a blue solution; but if the cobaltous salts are first oxidised to the "-ic" condition by such agents as Na_2O_2 in NaOH solution, they are insoluble and therefore may be completely precipitated as $Co(OH)_3$. See Donath, *Zeit. Anal. Chem.*, 1901, xl., 137.

Series VIII.—Precipitation of Manganese Peroxide by Chloric and Nitric Acids.

See "Ford's Method," Olsen's "Quant. Chem. Anal.," p. 385, 3rd Rev. Ed., and Ford, *Trans. Am. Inst. Min. Eng.*, ix., 397 and 100. Experiments were conducted to prove that the presence of Ni and Co do not interfere with the reaction formulated as follows:—

$$KClO_3 + HNO_3 \rightarrow HClO_3 + KNO_3$$
$$Mn(NO_3)_2 + 2HClO_3 \rightarrow MnO_2 + 2HNO_3 + 2ClO_2.$$

Small pieces of filter-paper were placed in the casserole with MnO_2 and boiled with HNO_3 (1 : 20); all of the MnO_2 dissolved in 10 minutes. 0·0003 grm. of Mn as $MnCl_2$ in 25 cc. of water yielded a comparatively voluminous precipitate.

Series IX,—Confirmatory Colour Test for Manganese.

Following the directions outlined in Procedure IV., it was found that 0·0002 grm. of Mn could be easily detected. The violet colour due to the presence of the MnO_4 ion is very distinct.

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O.$$

Series X.—Precipitation of Cobalt with Potassium Nitrite. Sensitiveness of Test.

0·0003 grm. of Co as $CoCl_2$ was treated according to Procedure VII.; the solution became turbid in 15 minutes. The experiment was repeated, using Ni instead of Co; the solution remained clear.

The above experiments were repeated, using 0·5 grm. of Co, and 0·5 grm. of Ni; results were the same.

See Procedure VII. and notes for further report.

Series XI.—Test for Nickel in Presence of Cobalt.

Following the directions given in Procedure VIII., 0·0003 grm. of Ni as $NiCl_2$ could be detected. A black precipitate, $Ni(OH)_3$ was obtained.

The experiment was repeated, except that 0·3 grm. of Co as $Co(NO_3)_2$ was used; no precipitate was observed.

Series XII.—Relative to the Accuracy and General Utility of the Proposed Method.

More than 100 students doing work in this laboratory in Qualitative Analysis during the past two years have used the methods proposed in this paper, and apparently have encountered no difficulties in following the procedures. Unknown mixtures particularly difficult of analysis have been given to the students in order to test the accuracy and utility of the methods. The instructor in charge of the work reports an unusually small percentage of failures. This is probably due to the fact that a moderate change in the conditions of precipitation does not greatly alter the accuracy of the methods.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

ORCHIDS AND THE EVOLUTION OF THE SPECIES.

For the last fifteen years a learned Frenchman, M. Noel Bernard, has been constantly studying the problem of the evolution of species that was, at one time, considered by many as inaccessible to laboratory methods, and reserved merely for the speculations of philosophers. By applying the Pasteurism methods to the study of the parasites of plants, M. Noel Bernard has, by decisive experiments, shown the preponderating *rôle* that have in all probability been played by microbian maladies in past millenniums in the evolution of vegetable species. This botanist has shown how one of the strangest flowers of our gardens, the orchid, cannot propagate unless the tiny seeds that fill the cavity of its fruit with an impalpable dust are attacked by parasitical fungi. The rudimentary seeds of the orchid are incapable of developing in the same conditions which suffice for the germination of other grains. M. Noel Bernard has reproduced in his laboratory diverse orchids. He has observed that living together with the fungi is imposed as a necessity to these perversely coloured flowers. Like Pasteur, Chamberland, and Roux, who showed that the virulence of bacteria can be increased, M. Noel Barnard has discovered a striking analogy of these phenomena in the case of orchids. By appropriate cultures the learned botanist has obtained far more active fungi than those that are normally met with, and capable of germinating a greater number of seeds of one seedling. From a general inquiry made concerning the parasitism of the higher grades of plants, MM. Noel Bernard, J. Magrose, and C. Bean have arrived at the conclusion that it is highly probable some state of vegetables must be considered as being, to a certain extent, the symptom of an infectious disease. Prof. Gaston Bonnier, in a notice that he read before the Academy in the name of M. C. Bean, has confirmed these researches. An orchid of our countries, the autumn spiranthis, has been the object of his studies. The germination of this orchid likewise cannot take place unless associated with a special filamentous fungi—the orchid gets rid of its associate to live separately. These experiments, which may find practical important application for the culture of all kinds of orchids, are susceptible one day of making biologists masters of the evolution of vegetable species.

CLOUDS AND TERRESTRIAL MAGNETISM.

An entirely new theory concerning clouds, advanced a few months ago by M. Birkeland, a learned Swedish physician, seems to be confirmed by a series of observations that an astronomer of the Lyons Observatory, M. Flajolet, has lately made on the *cirri*. These high clouds, that float at more than 9000 metres high, appear like parallel filaments, or turned over in the form of curls of hair. They often produce halos, and their apparition appears to be related to the variations of terrestrial magnetism. This concordance comes to support the hypothesis of M. Birkeland.

THE FLUVIAL AND GLACIAL HISTORY OF THE RHONE.

Few valleys have been the subject of more studies than the Valley of the Rhone in the neighbourhood of Lyons. Falsan and Chantre sought for the limits of the Rhodanian glacier in 1877. Recent researches have just been made by M. Ch. Duperet on the history of the Rhone in the Lyons region. They have been communicated to the Academy of Sciences by M. Douville. M. Duperet distinguishes two principal epochs, the period of pliocene alluviums, then that of quaternary alluviums. In the first, three terraces were formed, one 215 metres high; the second, from 140 to 145 metres high; the third, from 120 to 125 metres, this last against the Dombes. At the period of quaternary alluviums, M. C. Duperet has recognised a high terrace of from 90 to 95 metres that has been ravined to the bottom of the present valleys by the Rissien glacier. The Rhone glacier invaded the Lyonese region at the end of the quaternary period, consequently at a relatively recent epoch.

PLANTS CULTIVATED AT THE NEOLITHIC EPOCH.

It is generally admitted that the men of the age of hewn stone were exclusively hunters. With the invasions, probably of Asiatic origin, which brought into Europe a part of the Neolithics (dolichocephalic races) the manner of living changes; from pastoral it becomes sedentary. The Neolithics begin to raise domestic animals and to cultivate certain species of plants, the remains of which are to be found in the lake dwellings. Prof. Schenk has brought this question to an interesting point. Corn is the most ancient, or one of the most ancient, plants known. Prette and Boule have observed samples of it in the celebrated layer of the Mas d'Azil (Tourassian period or end of the hewn stone period). Corn is to be found in all the lake dwellings. It is identical to the Mottu corn still grown to-day (for straw for plaiting) in the Gruyère Valley, Canton of Fribourg. Zaborowski believes that this kind of plant is essentially of Asiatic origin. It would then have been brought into Europe by the dolicocephalic neolithic invaders. Egyptian wheat has also been found in several lake dwellings. Barley is also pretty frequent; it is represented by six very distinct varieties. On the other hand, rye and oats were known but were very rare. Flax was represented by a different kind from the present species, and which is still living to-day in a wild state in the Mediterranean basin. The other plants of the lake dwellings were probably gathered in a wild state. It was especially fruits which were generally cut in quarters and dried, such as certain little species of apples and pears; among these latter the present Swiss species of *Achras* has been found. Most of the wild fruit was consumed more or less accidentally. As to the origin of these neolithic species it does not seem that this question has progressed much since Heer and Candolle.

PURE OXYGEN FOR BLAST FURNACES.

The factories of Ougree-Marihaye began some few months ago to experiment on the use of pure oxygen instead of air in blast furnaces. The oxygen is extracted from the air by means of the Claude apparatus, well known to our readers. This substitution presents a great number of advantages; with oxygen it becomes unnecessary to force the combustive gas into the apparatus, the escapement gases in these conditions giving a greater quantity of heat, transformable into a motive form. It must be added that the functioning of the oxygen apparatus frees great quantities of pure nitrogen that can be utilised, for example, to manufacture nitrogenous manures. The experiments that have been made up till now have shown that the employment of oxygen would increase the production of the blast furnace very considerably (12 per cent), at the same time economising 5 per cent of coal.

Intervention of the Number Π in the Relations between Atomic Weights.—P. Dambier.—From the comparison of the atomic weights of certain elements it appears that these numbers depend upon one another by relations which involve the Number Π (3·141593). The author has arrived at this result by investigating the eight elements Cl, Br, I; C, N, O, S, and H. The following are some of the values of Π calculated by using the atomic weights of Guye:—

$$\frac{CN}{2CN - Cl} = \frac{\Pi}{2} \qquad \Pi = 3{\cdot}1415$$

$$\frac{HCl + 2\Pi}{NH_3 - 2\Pi} = 4 \qquad \Pi = 3{\cdot}1416.$$

—*Journal de Chimie Physique*, xi., 2.

NOTICES OF BOOKS.

Chemistry and its Relations to Daily Life. By Louis Kahlenberg and Edwin B. Hart. New York: The Macmillan Company. 1913.

This book is intended to provide a year's course of theoretical and practical chemistry for students of agriculture and home economy in technical schools. The authors have endeavoured to give a thoroughly sound and scientific presentation of their subject, and have succeeded in producing a work which will be specially suitable for agricultural students, and will give them a good grounding in the application of the principles of chemistry to problems in farming. For a single year's work too wide a region is covered, and there is perhaps rather too much detail; for example, some of the more complicated formulæ might well be omitted. The short course of laboratory work is well-planned and useful, and the use of different kinds of type in the text and the constant emphasis laid on important points ought to make it very easy for the student to get a good grasp of the salient features of the chemistry of everyday life.

The Chemistry of Rubber. By B. D. Porritt, B.Sc. (Lond.), F.I.C. London: Gurney and Jackson. 1913.

In this monograph the properties, constitution, and vulcanisation of rubber are briefly treated from the chemical point of view. A certain amount of space is devoted to the consideration of some matters of technical importance, but usually only in so far as it is necessary to be acquainted with them in order to obtain a clear grasp of the chemical questions involved. The evidence which has been accumulated as to the constitution of caoutchouc is clearly and impartially put before the reader, and the recent work which has been done on the synthesis of rubber and the preparation of isoprene is described. The chemist who is specially interested in the rubber industry will find the full bibliography very useful and the monograph will serve as an admirable introduction to the detailed study of the copious literature on the subject.

The Work of the Dominion Experimental Farms. By Frank T. Shutt, M.A., F.I.C., F.R.S.C. Toronto: The University Press. 1913.

The address printed in this pamphlet was read before the Canadian Institute, Toronto, in December, 1912. It contains a short history of the establishment of the five original Dominion Experimental Farms in 1866, and of the experimental stations which are the offshoots of them, and gives some account of the work which has been done in the several departments of these farms and stations. The author has thought it necessary to recapitulate some rather elementary and, one would have thought, well-known facts, such as the need for keeping stock and for the rotation of crops, but on the other hand he has some interesting remarks to make upon the results which have been collected in the investigations of different varieties of cereals. He also touches upon the research work done in horticulture, botany, and poultry keeping, and his report shows that the farms are doing a very valuable work, which is thoroughly appreciated by the farmers of the Dominion.

Les Propriétés Optiques des Solutions. ("The Optical Properties of Solutions"). By C. Chéneveau. Paris: Gauthier Villars. 1913.

This book is practically a new edition of the author's thesis on the same subject which was published four years ago. As in the original only two optical properties, dispersion and refraction, are discussed, but a very comprehensive account is given of the work which has been done on them. Some facts and theories of historical interest only have been omitted, to make room for a full discussion of recent results, and the author shows good judgment in the choice of his material. Thus, while he includes a certain number of experimental results, for fuller data he refers his readers to Tables of Physical Constants, and throughout the whole book he emphasises general principles without going into minute details. The determination of the constitutional formulæ of organic substances from the study of their optical properties is treated very satisfactorily, and the different types of apparatus employed in measuring refraction and dispersion are well described.

The Year-Book of Wireless Telegraphy and Telephony. 1913. London: The St. Catherine Press.

This year-book is the first work of its kind to be issued to the public, and there can be no doubt but that the increasing number of people who are interested either commercially or scientifically in wireless telegraphy will find it very acceptable. The editor had no easy task in meeting the very different requirements of these two classes of readers, but on the whole he has apportioned out his space judiciously, and there will be but few alterations in that respect to make before the next edition is issued. The Laws and Regulations of all countries are printed in full, and a complete list of all the wireless telegraph stations of the world, with call signals and other particulars, is given. The articles contained in the book deal with Wireless Time Signals, The Wireless Direction Finder, The Technical Situation of Radiotelephony, Wireless Telegraphy for Military Purposes, The Principles of Wireless Telegraphy Explained by Mechanical Analogies, &c. A dictionary of technical terms in five languages is included, and a catalogue is given of Applications for Patents in 1911 and 1912. The yearly record of progress in wireless telegraphy, which opens with the year 1896 might well have been taken a few years further back so as to include the suggestions and experiments of the true pioneers in this region, who foresaw the practicability of the application of the Hertzian waves in telegraphy, and pointed out in the clearest language what experiments were necessary in order that the then apparently impossible feat of transmitting messages by telegraphy without wires might be accomplished.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 3, July 21, 1913.

Action of Gaseous Hydrofluoric Acid on Quartz.—Armand Gautier and P. Clausmann.—The authors have found that hydrofluoric acid has hardly any action on the surface of quartz which is perpendicular to the axis, while the surface parallel to the axis is rapidly attacked. Similarly, the facets corresponding to the direct rhombohedron in a crystal are not attacked, while those corresponding to the inverse rhombohedron are etched, like the surface parallel to the axis. This is the first time it has been proved that there is a relation between the orientation of the different faces of a crystal, and hence the orientation of the molecules of which it is formed, and the energy of the chemical actions which the different facets undergo.

Tetra-alkylation of α- or 1-Methylcyclohexanone.—A. Haller.—The author has shown that the preparation of ethyl derivatives of cyclohexanone by means of sodamide gives very poor results, owing to the condensation of the ketone with itself. If, however, the fundamental ketone

ontains a methyl group the reaction becomes possible, and it occurs more easily the nearer the methyl is to the carbonyl group.

Composition of Essence of Coffee. Presence of Pyridine.—Gabriel Bertrand and G. Weisweiller.—Erdmann has found that an aqueous infusion of coffee contains traces of acetic acid and furfurol, appreciable amounts of valeric acid and furfurlc alcohol, a nitrogenous substance having the smell of coffee, and a certain proportion of phenolic substances resembling creosote. The authors find the substances mentioned by Erdmann do not when mixed give the aroma of infusion of coffee, and there is in the aqueous liquid a basic substance, which can be separated by means of silicotungstic acid, and proved to be pyridine. The amount of pyridine present is greater than that of all the other substances put together.

Action of Water on Carbides of Rare Earths.—A. Damiens.—When water acts on the carbides of cerium, lanthanum, neodymium, praseodymium, samarium, the chief gaseous products are acetylenic hydrocarbons. In addition hydrogen, ethylene, propylene and its homologues, ethane, propane, and butane are formed. No methane is ever produced. The acetylenic hydrocarbons include acetylene, allylene, and the vapours of heavier hydrocarbons. The oxides obtained are always sesquioxide hydrates, and the action is $C_2M + 3H_2O = M(OH)_3 + C_2H_2 + H_2$. The hydrogenation of acetylene gives ethylene and ethane.

Spontaneous Transformation of Hypochlorites into Chlorates and Hypobromites into Bromates.—J. Clarens.—When solutions of commercial hypochlorites are converted into chlorates no chlorite is formed. In solutions of hypobromites the presence of bromite can be detected before any bromate is formed. The following reaction first occurs : — $2KBrO = KBr + KBrO_2$. The bromite is then oxidised by the hypobromite as follows :— $KBrO + KBrO_2 = KBr + KBrO_3$, or else it is transformed into bromate, thus, $3KBrO_2 = 2KBrO_3 + KBr$.

Catalytic Preparation of Ketones by Oxides of Iron.—A. Mailhe.—The oxides of iron can conveniently be employed as catalysts to bring about the preparation of ketones from acids. Either ferrous oxide, obtained by heating oxalate of iron in a closed tube, or ferric oxide, obtained by the calcination of ferrous oxalate in air, can be employed. Ferric oxide is a particularly good catalyst. The worst yields are obtained with isovaleric and isobutyric acid. During the catalysis it is partially reduced to ferrous oxide, which itself possesses catalytic powers.

Action of Sodammonium on Phenylacetylene and on Styrolene.—Paul Lebeau and Marius Picon.—When phenylacetylene is hydrogenated with sodammonium the action does not stop at the corresponding ethylenic hydrocarbon, as in the case of the true acetylenic hydrocarbons of the fatty series, but the saturated hydrocarbon is also formed, namely, ethylbenzene. The intermediate ethylenic hydrocarbon, styrolene, is transformed into ethylbenzene by the sodammonium, with formation of sodamide.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 14, 1913.

Synthesis of Glucosides by means of Ferments.—Em. Bourquelot.—The author has shown that some ferments, *e.g.*, emulsin, are both hydrolysing and synthesising in their action, or, in other words, their action is reversible. There is a close resemblance between their action and the hydrolysis and formation of ethers. Thus, secondary alcohols more readily undergo both glucosidification and etherification than primary alcohols. The action is not limited only to those alcohols which are liquid at the temperature at which the ferments act. Certain organic compounds which are absolutely insoluble in water may, under the influence of ferments, form soluble compounds with glucose; this phenomenon is of great importance in biochemistry, for glucose is always present n living substances.

Determination of Copper by Methanal Sulphurous Acid.—Philippe Malvezin.—To prepare methanal sulphurous acid SO_2 is bubbled through a 40 per cent commercial solution of formol. The solution is standardised by titrating it with a solution containing 1 grm. of red copper in HNO_3, made up to 100 cc. To titrate, 1 cc. of this solution, 2 cc. of ammonia, and 1 cc. of distilled water are placed in a test-tube, and the acid is added from a burette until the deep blue coloration first becomes green and then the solution becomes colourless. This ought to take about 5 cc. of acid. To determine the copper in a substance about 0·1 grm. is gently heated, and the residue treated with HNO_3. The liquid is made up to 20 cc. with distilled water. Ten cc. are filtered off. Two cc. of ammonia are added, and the liquid is again made up to 20 cc. with distilled water, and filtered. Ten cc. of the new filtrate are taken for the titration, 1 cc. of ammonia being added. If n is the number of cc. used in the titration with the known copper solution $x = \frac{40 \times n'}{n}$, where n' = the number of cc. of acid actually employed.

MISCELLANEOUS.

Chemical Society.—An Extra Meeting of the Chemical Society will be held at Burlington House, Piccadilly, W., on Thursday, October 23, 1913, at 8.30 p.m., when the Ladenburg Memorial Lecture will be delivered by Prof. F. Stanley Kipping, D.Sc., F.R.S.

Institute of Chemistry.—Mr. W. P. Dreaper, F.I.C., will deliver the first of two lectures on "The Research Chemist in the Works, with special reference to the Textile Industry," on Wednesday, October 29th, 1913, at 8 p.m., at the Imperial College of Science and Technology, South Kensington, London, S.W.; Prof. Raphael Meldola, D.Sc., F.R.S., President, in the Chair. *Syllabus of Lectures*:—The British Textile Industry. Nature of training required for textile research. Conditions which govern investigation. Interpretation of results. Time and cost factors. Secret working. Improvements in plant and manufacturing operations. Originality an essential factor. Influence of local conditions on industry. Works research laboratory. Establishing experimental works. Nature of investigation. Study of detail a key to success. Mercerising and Schreinering. Value of observation. The chemist and the workman. Technology of textile fibres: Methods of manufacturing artificially prepared yarns and fabrics; their value in commerce; introduction of new fibres; variations in raw materials. Influence of theory. Is the action of dyeing, physical, electrical, or chemical? Chemical constitution and physical properties of fibres. "Neutral salt" reactions in presence of fibres, &c. Bleaching, dyeing, printing, and finishing operations. New dye-stuffs and their application. Silk weighting. Types of machinery used. Water supply. Special processes: Embossing, waterproofing, and gas-proofing fabrics; "cross-dyeing" effects; dyeing furs; action of heat and moisture, &c. The chemist and engineer. New processes and management of plant. Electro-bleaching. Electro-typing. Use of spray. Disposal of waste liquors. Development of textile research, and its systematic treatment.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Photographic Society, 8. "Photomicrography and Jam Adulteration," by E. Marriage.

THURSDAY, 23rd.—Chadwick Public Lectures, 5. (The University, Bristol). "Physiological Principles of Heating and Ventilating," by Dr. Leonard Hill.

—— Chemical, 8.30. The Ladenburg Memorial Lecture will be delivered by Prof. F. S. Kipping, F.R.S.

FRIDAY, 24th.—Physical, 5. "The Ice Calorimeter," by E. Griffiths. "An Electrostatic Oscillograph," by H. Ho and S. Kotô.

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THE SOLIDIFYING- AND MELTING-POINTS OF MIXTURES OF STEARIC AND OLEIC ACIDS.

By ROBERT MELDRUM

The following investigation was undertaken to confirm the degree of accuracy of Dalican's method of determining the solidifying-point and the thermometer bulb method of determining the melting-point of mixtures of fatty acids. As the same thermometer was used throughout, the investigation was a very prolonged and tedious one. As the readings and observations were made with great care, that is the main apology for their publication.

The solidifying-point and melting-point is the only means available of determining the degree of purity of innumerable organic compounds, and is also of importance in the examination of mixtures of fatty acids and organic mixtures having well-defined solidifying- and melting points. The use of the solidifying and melting-point methods may be further extended in analytical work by melting down 50 per cent of the sample with 50 per cent of some suitable non-volatile solvent such as aniline, oleic acid, sperm oil, or mineral oil, and determining the melting-point or solidifying-point at such dilution. But before such methods as these can be applied to comparative analysis it is necessary to know the limit of accuracy inherent in the methods of solidifying- and melting-point determinations in some standard mixtures, and that is the reason why stearic and oleic acids were selected for this work.

The solidifying-points were taken in a test-tube 7 inches by 1 inch, filled three parts full. Tubes of greater diameter have greater advantages over narrower tubes, as the cooling is slower, and there is more matter between the thermometer and walls of tube. The test-tube was passed through a bung fixed to glass jar. The thermometer used was a 60° C. divided into one-tenths. The mixtures were melted and cooled to 10° C. above their solidifying-point fixed in jar, and when crystallisation had commenced at bottom the whole was very slowly stirred till the thermometer ceased to fall, then thermometer was fixed in centre 1½ inches from bottom and the readings completed. The point at which the thermometer rose and remained stationary was called the solidifying-point. Five determinations were made of each mixture, the results being recorded below. The oleic acid used had solidifying-point 8° C., the stearic acid 54·8° C.

Solidifying-point by Constant Stirring Method.

Oleic acid. Per cent.	Stearic acid. Per cent.	Solidifying-point +rise °C. Min	Max	Avg.	Rise °C. Min.	Max.	Avg.	Difference in solidifying-point for each increment of 10 per cent oleic (°C.).
0	100	54·6	54·9	54·8	0·7	1·1	0·8	—
10	90	53·2	53·4	53·3	0·8	0·9	0·8	1·5
20	80	51·6	51·6	51·6	0·9	1·0	0·9	1·7
30	70	49·6	49·8	49·7	0·9	1·0	1·0	1·9
40	60	47·4	47·6	47·6	1·0	1·2	1·1	2·1
50	50	44·6	44·8	44·7	0·9	1·2	1·0	2·9
60	40	41·1	41·3	41·2	1·0	1·1	1·0	3·5
70	30	34·6	36·7	36·6	0·4	0·9	0·6	4·6
80	20	30·3	31·0	30·5	0·7	0·5	0·5	6·1

It will be seen from above that this method of constant stirring yields very concordant results for any given mixture; the maximum difference being 0·3° C. up to 70 per cent oleic, and increasing to 0·7° C. at 80 per cent. But this greater error is overbalanced by the greater difference in solidifying-point between 70 and 80 per cent oleic, which is 6·1° C. It is generally accepted that the accuracy of the solidifying-point decreases in proportion to its decrease; and this is the reason why the titre is seldom applied to low melting mixtures, as the determinations are treated as unreliable. But when we examine this point more closely we see that such is not the case, and, on the contrary, the low melting mixtures yield results more constant in accuracy than the high melts, as the following figures will show.

Difference in Solidifying-point for each Increment of 10 per cent Oleic (°C.).

A.	1·5	1·7	1·9	2·1	2·9	3·5	4·6	6·1

Limit of Accuracy (°C.).

B.	0·2	0·0	0·2	0·2	0·2	0·2	0·1	0·7

Percentage B *on* A (°C.).

13·3	0·0	10·5	9·5	6·9	5·7	2·1	11·4

These figures clearly show that with stearic acid the determination is only accurate to within 13·3 per cent, and with the 80 per cent mixture the accuracy is 11·4 per cent. But the important fact here brought out is that the error of accuracy decreases with a decrease in the solidifying-point. In other words, the softer mixtures give more reliable results. It will be observed that 10 per cent oleic acid only lowers the solidifying-point by 1·5° C., or 1 per cent = 0·15°, which is beyond the limit of accuracy of the test; 2 per cent oleic acid would only lower the solidifying-point by 0·30° C., the actual limit of accuracy. Whereas with the 80 per cent mixture a difference of 1 per cent oleic would affect the solidifying-point by 0·61° C., nearly the actual accuracy at that dilution. With the 70 per cent mixture each per cent oleic present = 0·46° C. It is therefore evident the more accurate the determination the lower the solidifying-point. That is why in two given samples, of the same solidifying-point, when melted down in some solvent and the solidifying-points determined, a difference at these dilutions will often be found between them.

With all solidifying-point determinations the number of degrees the thermometer rises and remains stationary are very important points, which will often yield to the analyst information not otherwise available. So far as these mixtures are concerned the maximum rise remains constant at between 30 and 60 per cent oleic acid. As the solidifying-point falls the "rise" increases, then remains constant, and again falls.

Another series of solidifications were made under the same conditions and the same apparatus and the same mixtures but *without* stirring, the thermometer remaining stationary all the time. The following are the results:—

Solidifying-point by Stationary Method.

Oleic acid. Per cent.	Stearic acid. Per cent.	Solidifying-point +rise. Min.	Max.	Avg.	Rise °C. Min.	Max.	Avg.	Difference in solidifying-point for each increment of 10 per cent. oleic.
0	100	53·6	53·9	53·7	0·2	0·3	0·3	—
10	90	52·2	52·4	52·3	0·3	0·5	0·4	1·4
20	80	50·8	50·9	50·9	0·7	0·8	0·7	1·4
30	70	48·9	49·0	49·0	0·7	1·0	0·8	1·9
40	60	46·4	46·6	46 6	0·5	0·9	0·7	2·4
50	50	43·6	43·7	43·6	0·7	0·8	0·8	3·0
60	40	39·8	40·1	39·9	0·5	0·1	0·7	3·7
70	30	35·3	35·6	35·4	0·4	0·6	0·5	4·5
80	20	29·2	29·4	29·2	0·3	0·6	0·4	6·2

By this method the readings agree within themselves by 0·3° C., the limits of accuracy, and confirm in all detail the results obtained by the first method. There are, however, two distinct differences between the methods. By the

stirring method the rise is higher and the solidifying-points are also higher, as will be seen from below :—

Average Rise in T° by both Methods.

Oleic.	Stirring.	Stationary.
Per cent.	°C.	°C.
0	0·8	0·3
10	0·8	0·4
20	0·9	0·7
30	1·0	0·8
40	1·1	0·7
50	1·0	0·8
60	1·0	0·7
70	0·60	0·5
80	0·5	0·4

Here it is clear the quicker the cooling the higher the rise. The rise is apparently governed by the amount of matter crystallised per interval of time. With solidifying point determinations it is the usual custom to include the "rise" in the solidifying-point, as the solidifying point is the highest temperature at which solidification takes place, and is well-defined, due to the thermometer remaining stationary for long periods at that point. Thus,—

Per cent oleic acid	0	10	20	30
Minutes thermometer remains stationary	30	20	12	12

But then, again, the lowest temperature to which a liquid must be cooled to produce a homogeneous solid may also be stated to be the true solidifying-point. The most troublesome part of the "rise" is that it is far from constant, varying in any series as much as 0·5° C. But most likely this is due to the commencement of the rise not being well-defined and erratic. This point requires further investigation as it is of some importance. Where the solidifying-point of a substance having no "rise" requires to be compared with another having a "rise" of 1° or 2° C. the comparison is very troublesome and confusing. But "rise" or no "rise" the point is well-defined in both cases where the thermometer remains for the longest period stationary. Some stearic acid was melted in test-tube and this plunged in cold water; the solidifying-point indicated was 53·9° C. with a rise of 0·3° C. In another experiment 200 grms. of a 10 per cent oleic acid and 90 per cent stearic acid were placed in glass ball, the thermometer placed in centre and allowed to cool. The T° fell to 51·8° C, and remained for over 30 minutes at that without showing a "rise." This only indicates the troublesome nature of the "rise" which depends on thermal conditions, which may or may not be present at any given time. The rise is apparently eliminated when working with large quantities, due to the slow rate of cooling. It seems to me the direction in which the "rise" is likely to be eliminated from the test is by conducting the solidification in a hot water jacket. It will be apparent that to eliminate the "rise" would not affect the longest interval at which the thermometer remains stationary, but would lower all the readings.

Of the two methods the stationary method yields the lower results uniformly through the whole series as follows :—

Oleic.	Stirring.	Stationary.	Difference.
Per cent.	°C.	°C.	°C.
0	54·8	53·7	1·1
10	53·3	52·3	1·0
20	51·6	50·9	0·7
30	49·7	49·0	0·7
40	47·6	46·6	1·0
50	44·7	43·6	1·1
60	41·2	39·9	1·3
70	36·6	35·4	1·2
80	30·5	29·2	1·3

This difference is not due entirely to the difference in "rise," but most likely is due to rapidity of crystallisation. The methods show, with stearic acid alone, a difference of 1·1° C., which is equivalent to about 7 per cent oleic acid. The question is which method approximates the true solidifying point, and from our foregoing argument there can be no hesitation in determining that to be the stationary method.

The relationship between the solidifying point and melting point is generally somewhat obscure, the general idea being that the melting-point is always higher than the solidifying-point. The author's experience extending over the past twenty years confirms that, working with a varied assortment of substances and various melting-point methods. But it would appear that the ratio between the melting-point and solidifying-point depends on the melting-point method used, there being no definition of what the actual melting-point really is. A series of determinations were made of the melting-point by the thermometer bulb method, using the same thermometer and the same mixtures of stearic and oleic acid as used for determining the solidifying-point. The thermometer was dipped into the melted fat at about 10° C. above its melting-point; and with the low melting mixings the thermometer was cooled down to 0° C. before dipping to obtain a uniform coating throughout the series. The thermometer was fixed in test-tube $\frac{3}{4}'' \times 7''$, fixed in beaker of water, and heated gradually while stirring the water. So far as these mixtures are concerned, cooling the thermometer down for twenty-four hours after coating with fat and thirty minutes cooling, no difference was found in melting-point. Cooling down quickly at 0° C. and at 15° C. no difference in melting-point was observed. Numerous observers have frequently pointed out the importance of prolonged cooling, and have obtained differences in the melting-point of several degrees when rapidly cooled. So far as this method is concerned, constant results depend not on the rate of cooling but on the uniform coating of the thermometer bulb. If the coating is too thin the melting-point is likely to be high, due to the fact that the temperature of fat must be increased above its actual melting-point to produce sufficient viscosity to cause it to flow into a bead. On the other hand, when the film is too thick the fat begins to flow and forms beads below its melting-point, as numerous, if not all, solids flow below their melting-point, but in all these cases opacity is present. The following determinations were made with the greatest possible care, five being made for each series :—

Melting-point by Thermometer Bulb Method of Mixtures of Stearic and Oleic Acids.

Oleic acid	Stearic acid	Melting-point °C.			Difference for each 10 per cent oleic.
Per cent.	Per cent.	Minimum.	Maximum.	Average,	
0	0	55·4	55·8	55·6	—
10	90	53·8	54·0	54·0	1·6
20	80	52·1	52·6	52·3	1·7
30	70	49·8	50·4	50·1	2·2
40	60	47·5	47·8	47·6	2·5
50	50	45·2	45·3	45·3	2·3
60	40	42·0	42·5	42·3	3·0
70	30	37·8	38·2	38·1	4·2
80	20	32·8	33·4	33·0	5·1

This method it will be seen is only accurate within 0·5° C. for all the series. The following shows the difference between the melting-point and solidifying-point by stationary method :—

	Melting-point.	Solidifying-point.	Difference.
Per cent.	°C.	°C.	°C.
0	55·6	53·7	1·9
10	54·0	52·3	1·7
20	52·3	50·9	1·4
30	50·1	49·0	1·1
40	47·6	46·6	1·0
50	45·3	43·6	1·7
60	42·3	39·9	2·4
70	38·1	35·4	2·7
80	33·0	29·2	3·8

The curious fact is that there is a decrease in difference between the melting-point and solidifying-point from 0° to 40 per cent, and then an increasing difference for the remainder of the series. The melting-points approximate more closely to the solidifying points by the stirring method as follows :—

Oleic. Per cent.	Melting-point. °C.	Solidifying-point. °C.	Difference. °C.
0	55·6	54·8	0·8
10	54·0	53·3	0·7
20	52·3	51·6	0·7
30	50·1	49·7	0·4
40	47 6	47·6	0·0
50	45·3	44·7	0·6
60	42·3	41·2	1·1
70	38·1	36·6	1·5
80	33·0	30·5	2·5

The differences here are lower than by the stationary method. At the 40 per cent mixture the difference is least, being equal to each other. The melting-point of the 10 per cent mixture was determined by the capillary tube method, which yielded readings as follows :—52·6, 51·8, 52·4, 52·2 ; average = 52·2° C. Here it will be noted the melting-point is lower than the solidifying-point by either method, and nearly 2° lower than the melting-point method by thermometer bulb.

The melting-point of stearic acid was determined by a new method not hitherto published. U-tubes with 12 cm. legs by 2·5 mm. bore by 1 mm. thick were used. The stearic acid was melted and sucked into leg, and when cold end of U-tube was heated to melt out 6 cm. of the fat, leaving a column of 4 cm. in leg. The thermometer was placed between legs, and the U-tube immersed in water and heated at rate of 0·5° C. per minute while stirring. The temperature at which both columns of fat are of equal height is the melting-point. The figures obtained were :—55·4, 55·4, 55·5, 54·6, 55° C. ; limit of accuracy, 0·9° C. The fat remains opaque even when maintained at a temperature of 56° C. for thirty minutes, and only clarifies when heated to 57·8° C. The inherent weakness of this process is that the fat flows while still opaque. Another method was tried by using straight tubes 12 cm. long by 2·5 mm. bore by 1 mm. thick. In this case the tube is dipped into melted fat to the extent of 4 cm., finger placed on top and removed, and allowed to cool. This tube is now fixed to thermometer with india-rubber band and placed in beaker of water heated at rate of 0·5° C. per minute while stirring, the water level being 4 cm. above fat. The temperature at which the column ascends is the melting-point. This method gave :—53·8, 53·8, 54·4, 53·8, 53·8, 54·0, 54·4° C. ; limit of accuracy, 0·7° C. The defect of this method is that the column of fat commences to ascend while still solid and opaque, due to the fact that the core of fat becomes fluid on outside, leaving a solid core inside. Another objection is that the movement of the fat depends on pressure. The process, however, yields very constant results. The ordinary capillary tube method gave :—54·8, 55·4, 55·6, 55·2 ; error of accuracy, 0·8° C.

The following is a summary of these melting-point determinations :—

	Min.	Max.	Avg.	Limit of accuracy.
Thermometer bulb	55·4	55·8	55·6	0·4° C.
U-tube	54·6	55·5	55·2	0·9° C.
Straight tube ..	53·8	54·5	54·1	0·7° C.
Capillary tube ..	54·8	55·6	55·2	0·8° C.

According to these determinations the bulb method is the most accurate, yielding the most constant results with least variation. By the four methods the melting-point is in each case higher than the solidifying-point, and as is well known the melting-point varies according to the method used. It therefore would appear that the melting-point is only apparently higher than the solidifying-point, due to all melting-point methods yielding too high results.

PRODUCTION OF HYDROCARBONS FROM A SOLUTION OF SODIUM STEARATE BY ELECTROLYSIS.

By H. T. F. RHODES.

As is well known, it is possible to produce ethane by the electrolytic dissociation of potassium acetate—

$$\begin{array}{llll} CH_3 & COO & K + HO & H \\ + & & & - \\ CH_3 & COO & K + HO & H \end{array}$$

As the number of carbon atoms rise dissociation by electrolysis becomes more difficult. Probably the cause of this in the case of sodium stearate, and the salts allied to it, is the partial hydrolysis which takes place when these salts are dissolved in water. It has been found possible, however, by using a very low current, to dissociate an aqueous solution of sodium stearate.

Three grms. of pure hard soap, consisting entirely of sodium stearate, were dissolved in 100 cc. of water. The solution was acified with acetic acid, and electrolysed for fourteen hours, using 0·3 ampère. The solution was then diluted with water, and was allowed to stand for a week ; it was then filtered, and a small quantity of a hydrocarbon very similar in physical properties to paraffin wax was obtained. It is interesting to note that the hydrocarbon could not be detected in the solution until it had stood for some considerable time. It was probably in a very fine state of division immediately after electrolysis.

The data is not very satisfactory, as reliable results were obtained on two occasions only, and in each case the yield was so small that it was impossible to definitely decide its exact composition.

NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

(Continued from p. 182).

II. *The Objections Urged against the Existence of Liquid Crystals.*

Herr Mlodziejowski, who disputes the existence of liquid crystals (*loc. cit.*), did not perform the experiments described above. He merely allowed the solution (containing excess of water) obtained by his method to evaporate under the microscope, when naturally the composition of the solution was continually changing and important complications must arise at the free surfaces owing to the effect of surface tension.

From similar observations of *uncovered* solutions, M. Vogelsang ("Die Kristalliten," Bonn, 1875) had already arrived at the erroneous conception of the existence of attraction forces of crystals by means of which they can influence other crystals which are free to move, just as magnets can attract and arrange other magnets. For the same reason Herr M. had no difficulty in explaining by means of hypothetical forces the anisotropism and clustered formation of the structures observed by him, as well as the phenomenon of again assuming their normal structure when they flow together ; these forces are supposed to be exerted upon one another by invisibly small solid crystals of anhydrous ammonium oleate when they are suspended in oleic acid. But such mysterious actions at a distance between crystals are unknown in physics ; even with crystals molecular forces act only at molecular distances.

According to G. Quincke (*Wied. Ann.*, 1894, liii., 615), who is the originator of this theory after Herr M., the directive forces which the crystals experience proceed from the surface skin of the oleic acid. These influence soap

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

crystals just as a thin layer of mica affects little crystals of potassium iodide, and forces them to arrange themselves in definite positions. But only the hypothetical layer of invisible tiny crystals lying close to the surface could be thus arranged, and the arrangement would not be that which is actually observed. For with simple liquid crystals the extinction between crossed Nicols is absolute; the molecular axes can thus form all possible angles with the surface, whereas they should be perpendicular to it. Herr M.'s hypothesis moreover provides no explanation of the fact that the smallest simple crystals always exhibit the form of an extended tetragonal octahedron or its growing form (more projecting edges), and thus possess an axis of symmetry of the second order (except in the case of the rounding of the surface, which is also to be seen in many soft solid crystals of simple structure, like ammonium chloride, silver iodide, camphor, &c.). What force could then produce four projections (90° apart) in the drops of oleic acid drawn out longways into the shape of a spindle (by some inexplicable force), and moreover always four projections and never one or two or three? This phenomenon can only be explained on the assumption that the smallest crystals, which have been undisturbed during growth, have a lattice structure like solid crystals.

The disappearance of the parallelism of the secondary axes when the crystals flow together is due to the fact that, as the phenomenon of forced homotropism shows, the molecules can turn very easily about the principal axis (optical axis). The molecules must be regarded as leaflets which endeavour to become parallel when the crystals flow together, but remain irregularly arranged as regards the direction of the secondary axes, so that the resulting semi-isotropic structure possesses an unlimited number of planes of symmetry through the principal axis. Of the eight projections which two crystals flowing together possess, two could easily disappear, so that only six remain, which at once arrange themselves symmetrically. They no longer correspond to a lattice structure, but produce disturbances of the semi-isotropic structure. From the flowing together of more crystals, structures with 10, 14, or more projections could result. This fact is in good agreement with the theory of liquid crystals.

Another mystery, the explanation of which Herr M. leaves to the reader, is the fact that the hypothetical crystals of anhydrous ammonium oleate suspended in the drops of oleic acid have such minute dimensions that they are invisible even when magnified by the strongest microscope, while this salt when it crystallises from oleic acid appears as distinct crystals which can easily be recognised when slightly magnified. This mystery will never be explained, for owing to the large amount of water in Mlodziejowski's preparation it has been proved above that crystals of anhydrous neutral ammonium oleate could not be formed in the drops of oleic acid. If there could be any question of solid crystals, they would be crystals of acid ammonium oleate hydrate, which, however, as has already been said, are very large. Even if we disregard this contradiction of experience we are at once confronted with a new mystery.

What explanation could be given of the fact that the drops of oleic acid remain unchanged in an aqueous solution saturated with ammonia? As has already been pointed out, an excess of ammonia is very favourable to the formation of liquid crystals, while lack of ammonia prevents their formation and converts all the crystals that have been formed and the oleic acid into solid acid ammonium oleate. Herr M.'s article provides no answer to these questions, which he naturally does not suggest, being ignorant of the facts. If Herr M. had tried to destroy the supposed drops of oleic acid, *i.e.*, the liquid crystals, by the addition of gaseous ammonia, he would have observed, in contradiction to his theory, that the liquid crystals were *not* destroyed, but that, on the other hand, they appeared more stable the greater the excess of ammonia.

Herr M. does not explain why the "chrysalis-like" structures of oleic acid and solid crystals of ammonium oleate look exactly like the liquid crystals of other chemically well-defined substances, in the case of which a decomposition into solid crystals and an oily isotropic liquid is precluded for chemical reasons. According to his observations the oleic acid can be pressed out of the liquid crystals, and often even flows out of them of its own accord in the form of a drop. Here, again, there is an error. For if the structures in which this was observed were actually those called liquid crystals by me it would simply be a case of an optical illusion depending upon the phenomenon that crystals, one end of which touch the glass of a slide, suffer a change of structure so that all the molecular axes become perpendicular to the glass (see *Heidelberg Sitzungsber.*, 1911, No. 22, Table II., Fig. 16 *a—c*) (Note 5). The supposed drops of oleic acid are nothing but a part of the crystal which has become pseudoisotropic and has spread out in little round discs on the glass.

Thus no objections to the explanation of the structures observed as being liquid crystals can be regarded as tenable. They are all in direct opposition to the actual facts. On the other hand, the theory of liquid crystals is not contradicted by a single *fact*, but only by a *hypothesis*, namely, the assumption that the molecules of all so-called modifications and states of aggregation of a substance are identical. It is certainly quite irreconcilable with this assumption (*Zeit. Phys. Chem.*, 1910, lxxi., 355; *Verh. d. Karlsr. Nat. Ver.*, 1913, xxv.). But this only demonstrates the incorrectness of the hypothesis, which may also be deduced from other facts ("Molecular-physik," 1889, ii., 413).

III. *Structure and Form of Liquid Crystals.*

If we bend a sheet of mica, in consequence of the distortion of the molecules or the alteration of their distances, elastic reaction force comes into evidence, and lasts as long as the bending, disappearing when it comes to an end, since inasmuch as the limits of elasticity were not passed the grating arrangement of the molecules remained the same. When a liquid crystal is bent such a lasting elastic reaction force never comes into play; for if by the bending the molecules are momentarily displaced the original grating arrangement is at once spontaneously restored by the action of the molecular directive force, even if the crystal is not bent back. Crystals which flow together thus possess no limits of elasticity, and for this reason must be called "liquid"; for the lack of a limit of elasticity is the special characteristic of the liquid state.

The molecular directive force not only restores the disturbed structure of liquid crystals, but also their altered form. If a piece is broken off a solid crystal the molecular forces cannot fill up the gap, if the crystal is not suspended in a supersaturated solution in which it can again become perfect by the addition of new material. A liquid crystal, on the contrary, at once resumes its normal form, in which equilibrium is restored between the molecular forces among themselves and the thrusts resulting from the thermic state of motion.

I have not yet succeeded in demonstrating this thermic motion in the usual way by observation of the Brownian movement (Rob. Brown, *Pogg. Ann.*, 1828, xiv., 294; J. Perrin, "Les Atomes," Paris, Alkan, 1913; O. Lehmann, *Verh. d. Karls. Nat. Ver.*, 1913, xxv., 41) because it is impossible to obtain little particles continuously in suspension in crystalline liquids. Thus, if an uncovered preparation of para-azoxyphenetol is slightly blackened over a turpentine or magnesium flame, and is then melted under a cover-glass, the Brownian movement among the particles of soot can readily be observed in the isotropic melt. But as soon as the conversion into a crystalline liquid occurs the particles of the growing liquid crystals are driven against the glass walls and remain suspended there, even if the mass is rubbed off in order to try to drive them again into the interior. The experiments of Friedrich, Laue, and others on the bending of the Röntgen rays in crystals (see also M. de Broglie, *Comptes Rendus*, 1913, clvi., 1011, 1153; M. Laue, *Phys. Zeit.*, 1913, [3],

xiv., 423) provide no evidence of thermic movement in them, and it must be assumed that it is negligibly small. Small very rapidly changing etched figures which I observed in the case of para-azoxyphenetol (*Phys. Zeit.*, 1911, xii., 543) might be caused by the state of thermic motion in the corrosive melt. The scintillating polarisation discovered by Ch. Mauguin (*Comptes Rendus*, 1912, cliv., 1359) in semi-isotropic liquid crystalline layers of optically biaxial substances, might be caused by the rapid change of the directions of the secondary axes, while the principal axes or axes of revolution of the molecules which are in the direction of the optical axes remain parallel, as shown by the complete extinction (in a capillary tube) when observed transversely.

Perhaps the thermic movement, *i.e.*, the expansive force, if it exists is anisotropic in the case of liquid crystals, and thus the surfaces turn outwards more forcibly in different places, until the capillary pressure aroused by the dilation again restores equilibrium. The form of a liquid crystal would then be the result of the opposing action of molecular forces and expansive force. On the other hand, that of a solid crystal would be the result of the repelling, attracting, and directing molecular forces. If this is correct the shapes of the liquid crystals must be fundamentally different from those of the solid crystals, which does not appear to be the case. Probably the force which determines the shape of the liquid crystals depends entirely upon the action of the so-called molecular forces, which is certainly difficult to understand from the point of view of the kinetic theory (Note 6).

From the behaviour, already described, of ammonium oleate in capillary tubes, it may be concluded that the molecules are not rod-shaped (in the direction of the principal axis) but leaflet-shaped (perpendicular to the principal axis), since rod-shaped molecules would arrange themselves obliquely to the walls when the mass was poured, owing to the greater velocity in the neighbourhood of the axis of the tube (Note 7). This formation of the molecules is confirmed by the phenomenon that even the power of adsorption of glass or mica plates is capable of producing semi-isotropic structure (*Ann. Phys.*, 1900, ii., 689; 1906, xix., 408; *Phys. Zeit.*, 1910, xi., 575; *Heidelb. Sitzungsber.*, 1912, No. 13, Table II., Fig. 21; F. Wallerant, *Comptes Rendus*, 1906, cxliii., 555; P. Gaubert, *Ibid.*, 1907, cxlv., 722; D. Vorländer, *Zeit. Phys. Chem.*, 1907, lxi., 166; D. Vorländer and H. Hauswaldt, "Acta nova," Halle, 1909, 90). It may be supposed that it compels the molecular discs to arrange themselves parallel to the surface of the plates, *i.e.*, so that the optical axes are perpendicular to the glass. This is confirmed by the fact that this alteration of structure is facilitated by pressing the mass between two plates or by gently pushing one over the other.

The effect of more powerful surface tension, such, for example, as is exerted at the surface exposed to the air, causes the molecular leaflets to arrange themselves parallel to the surface (*Ann. Phys.*, 1903, xii., 332; "Flüssige Kristalle," 1909, Table IX., Figs. 2 and 3).

The assumption that the molecules are disc-shaped is in good agreement with the phenomenon called forced homotropism, viz., when liquid crystalline layers flow rapidly over one another the molecules behave to a certain extent like furniture castors, the axes of which endeavour to become perpendicular to the direction of pushing. The mass thus becomes semi-isotropic in such a way that the optical axis is perpendicular to the direction of thrust, and the inner friction decreases as if the molecules acted as friction wheels, like the resistance of a wheelbarrow provided with guiding wheels, as soon as the wheels have arranged themselves properly (*Ann. Phys.*, 1903, xii., 318; *Zeit. d. Ver. D. Ing.*, 1908, lii., 387).

The spontaneous homotropism of liquid crystals when they flow together (*Zeit. Phys. Chem.*, 1895, xviii., 91) may be explained by supposing that the more or less irregularly arranged discs as they rub against one another exert directive forces on one another in such a way that they all take up the same orientation, at any rate as regards their surfaces. If, as with viscous liquid crystals, the arrangement of the individuals is not too irregular, fan-like structures must be produced, as with the solid crystals of acid ammonium oleate hydrate which has actually often been observed (*cf.*, O. Lehmann, "Flüssige Kristalle," 1904, Table I., Fig. 6; Table II., Fig. 1). This constitutes a transition to the sphaerolithic structure (*Wied. Ann.*, 1895, lvi., 784) which occurs in liquid crystals of ammonium oleate hydrate, if the solution contains much water, partly on account of the increase of surface tension thus produced, and partly on account of the decrease of viscosity (true stiffening) in consequence of the absorption of water (swelling up).

Also when liquid crystals of ammonium oleate are bent fan-like structures appear, inasmuch as on the concave side the molecular axes (directions of extinction) arrange themselves tangentially to the curve of bending, just as when a solid crystal (of, for example, ammonium nitrate, *Zeit. f. Kristallog.*, 1877, i., 110) or orthomercury-ditolyl (*loc. cit.*, 1885, x., Fig. 39) bends. The other molecules then endeavour to become parallel to them, and thus the fan structure is produced.

Allied to these fan structures are the conical and double conical structures (*Wied. Ann.*, 1895, lvi., 786, Figs. 20—26; *Ann. Phys.*, 1903, xii., 329; "Flüssige Kristalle," 1904, p. 40, Table V.; *Ann. Phys.*, 1906, xix., 408, Figs. 1—12; *Verh. d. Phys. Ges.*, 1911, xiii., 338; *Heidelb. Sitzungsber.*, 1911, No. 22, Table IV., Fig. 24; "Die neue Welt der flüssigen Kristalle," 1911, p. 368), which also produce molecular states of equilibrium, which in spite of thermic motion are permanent, and after any distortion of the mass (if it is not too deep-seated) again return to their original form as soon as the strain is removed. In spite of thermic motion they also are permanent, as the arrangement of the molecules corresponds to the molecular directive force, although the molecules are not parallel as in the grating structure or the state of semi-isotropic aggregation. They may be regarded as fan-structures which, being closely connected with one another, are grouped quite symmetrically about an axis, so that if the fan-structure can be explained on the ground of the hypothesis of the leaflet shape of the molecules and their behaviour as astatic systems of magnets (which has not yet been proved mathematically) the explanation of the conical disturbances on the basis of the same hypothesis offers no difficulties. The same holds good for the spiral structures which are produced in uniformly liquid crystalline layers by twisting the limiting anisotropic plates over one another, and also by addition of different non-isomorphic substances (Ch. Mauguin, *Comptes Rendus*, 1910, cli., 886; O. Lehmann, "Die neue Welt der flüssigen Kristalle," 1911, p. 222; *Ann. Phys.*, 1900, ii., 670; "Flüssige Kristalle," 1904, Tables XIV.—XVII.; *Ann. Phys.*, 1905, xviii., 808; *Phys. Zeit.*, 1911, xii., 540; *Ann. Phys.*, 1911, xxxv., 193; 1912, xxxix., 105; *Heidelb. Sitzungsber.*, 1912, No. 13, Table III., Fig. 64).

Speaking generally, we can say, at any rate as far as the hydrate of ammonium oleate is concerned, liquid crystals behave as if they consisted of mobile but approximately rigid leaflet-shaped molecules, which exercise turning moments (couples of forces) upon one another, comparable with those of astatic systems of magnets formed of revolving electrons (in paths which form knots).

Notes.

5. In view of the large amount of water in Herr M.'s preparations it might be thought that hollow liquid sphaerocrystals were observed, the interior of which was filled with isotropic mother-liquor, which can be pressed out if the crust has been converted into solid acid oleate by evaporation of ammonia from the solution. But the substance squeezed out is aqueous solution, not oleic acid.

6. For models to illustrate this, assuming the electromagnetic theory, see "Molecularphysik," 1889, ii., 376;

Phys. Zeit., 1909, x., 553; 1912, xiii., 550; "Die neue Welt der flüssigen Kristalle," 1911, 346.

7. If they were only systems of revolving electrons as shown by the models mentioned above they could be regarded as deformable. In this case the properties of a substance must be altered by deformation, which is not actually the case. But they can behave like rigid discs only if the velocity of motion of the electrons is very great. The phenomena of radio-activity actually reveal such great velocities in the interior of the molecule.

(To be continued).

THE FILTRATION OF BARIUM SULPHATE.

By J. L. OSBORNE.

KRAK (*Chemist Analyst*, 1912, p. 26) has recently stated that to filter barium with suction seems a rather daring experiment, even when specially prepared filters are used, but that it may be done as follows:—

"Pour the supernatant liquid through the filter, using suction. Before the precipitate begins to follow, add about 10 cc. of a saturated, slightly acid, solution of ammonium acetate to the precipitate, and stir it up well. The fine $BaSO_4$ changes instantly into a coarse precipitate, and can be washed instantly while suction is going full speed without ever passing through the filter. The results thus obtained are not influenced by the use of the filter solution."

This sounded as though the barium sulphate were coagulated by the ammonium acetate solution. It seemed desirable to verify this and to see what would be the effect of adding solid ammonium acetate to a solution from which barium sulphate had been precipitated cold. A number of experiments were therefore made to determine what happens and what are the limitations of the method, if any.

Equivalent solutions of barium chloride and of sulphuric acid were prepared, and 100 cc. of the barium chloride solution were added a little at a time to 100 cc. sulphuric acid, stirring continuously, and keeping the solutions at 75—80°. The precipitate is coarse enough for ordinary filtration by gravity, but is sucked through a filter-paper when suction is applied. In the next experiment the supernatant liquor was decanted, as recommended by Krak, and 10 cc. saturated ammonium acetate solution were stirred up with the residue. There seems to be a solution of the barium sulphate which re-precipitates as coarser crystals which are not carried through a filter-paper by suction. There is no difficulty at all in duplicating Krak's result.

In another experiment the barium sulphate was precipitated hot as before, but the supernatant liquid was not decanted. About 75 grms. of solid ammonium acetate were added to the solution, making the concentration with respect to this salt practically the same as in the preceding experiment. Filtration by suction was not possible. The whole mixture was boiled for nine to ten hours, but even then the barium sulphate ran through the filter under suction. This showed that a mixture of ammonium acetate and hydrochloric acid behaves quite differently from ammonium acetate alone. This might be due to the free acid or to the chloride preventing the growth of the crystals, or it might be that the chloride had a peptonising action and disintegrated the barium sulphate.

A hot solution of ammonium sulphate was precipitated by adding just sufficient hot barium chloride solution. Since there were about 110 cc. of solution, approximately 100 grms. of solid ammonium acetate was added, and the mixture was boiled for eight hours, four hours at a time with several hours of standing between the two periods. The barium sulphate could then be filtered with suction. This experiment shows that ammonium chloride retards but does not prevent the growth of the barium sulphate crystals.

Some barium sulphate was made filterable by Krak' method. This was boiled for nine hours with an ammonium chloride solution. At the end of this time the crystals filtered as well as before, thus showing that the ammonium chloride solution had no peptonising or disintegrating action.

To delermine whether Krak's method worked well with neutral and acid solutions, three sulphate solutions were made up of the same strength, sodium sulphate, sodium sulphate acidified with hydrochloric acid, ammonium sulphate. These solutions were heated to 80°, and sufficient hot barium chloride solution added to ensure complete precipitation. The mixtures were brought to boiling for five minutes, and were then allowed to stand over night. In each case the supernatant liquid was decanted, 5 cc. of saturated ammonium acetate added, and the solution boiled for five minutes. The precipitates did not filter well, so 10 cc. more of ammonium acetate solution were added to each beaker. Each solution was boiled for one minute, and then allowed to stand. There was no difficulty in filtering with suction, the three lots behaving practically alike.

The last experiments dealt with cold precipitation of sulphuric acid by barium chloride. After decantation, ammonium acetate solution was added, and boiling was kept up for eight to ten hours. It was quite impossible to filter the barium sulphate. The experiment was repeated with 20 cc. ammonium acetate solution, boiling steadily for ninety-six hours, using a reflux cooler. At the end of this time the barium sulphate filtered nicely with full suction.

These experiments clear up the theory of the process. Barium sulphate is soluble in ammonium acetate solution, and the crystals therefore grow in a hot solution. If the barium sulphate is precipitated under conditions such that the crystals are nearly large enough to permit of filtration with suction, a short heating is enough to make them grow to the required size. If the barium sulphate is precipitated cold, the crystals are small, and a very much longer heating is necessary to give the required size. Since ammonium chloride and hydrochloric acid do not peptonise or disintegrate the barium sulphate crystals and yet do retard the growth, it is clear that these substances decrease the solubility of barium sulphate in ammonium acetate solutions.

This work was suggested by Prof. Bancroft, and has been carried on under his supervision.—*Journal of Physical Chemistry*, xvii., No. 7.

A STUDY OF THE METALLIC TELLURITES.*

By VICTOR LENHER and EDWARD WOLESENSKY.

SINCE the early work of Berzelius very little has been contributed to the chemistry of the tellurites (*Jahresb.*, 1833; *Pogg. Ann.*, 1833, xxviii., 396; *Kongliga Svenska Vetenskaps Akademiens Handlingar*, 1833, 277; *Pogg. Ann.*, 1834, xxxii., 1—577; *Ann. Chim. Phys.* [2], 1835, lviii., 225). What work has been done has been largely incidental rather than a systematic study.

In our work the tellurites of potassium, sodium, silver, barium, magnesium, cadmium, nickel, cobalt, manganese, lead, and ammonium were studied. In addition to the normal tellurites, the di- and tetratellurites of the alkali metals were also studied. The normal and ditellurites of potassium and sodium were prepared by fusing tellurium dioxide with the calculated quantities of the alkali carbonates. The tetratellurites of potassium and sodium were obtained by the decomposition of the corresponding ditellurites with water. The tellurites of the other metals were prepared by precipitation from solutions of their salts (usually the chlorides) by means of sodium tellurite.

* *Journal of the American Chemical Society*, xxxv., No. 6.

The tellurium dioxide used was prepared from elementary tellurium by solution in aqua regia and precipitation from the hydrochloric solution by sodium bisulphite. The impure tellurium thus obtained was fused with an excess of potassium cyanide, the fusion extracted with hot water, when a solution was obtained of potassium telluride, selenocyanate, and thiocyanate. The insoluble residue was invariably refused and treated again as before.

Air was then bubbled through the solution, precipitating the tellurium, while the seleno- and thiocyanates were unaffected. The tellurium, after filtering and washing, was dissolved in dilute nitric acid and re-crystallised as the basic nitrate. The nitrate was finally heated strongly in a platinum crucible, and tellurium dioxide obtained. The dioxide was then fused, to insure complete removal of oxides of nitrogen. The product was perfectly white.

Methods of Analysis.

In the analysis of the tellurites studied, the following methods were used. Water was usually determined by loss of weight on heating. In some cases a temperature of 450° was necessary for the complete dehydration of the substance, but in such cases it was not necessary to continue the heating for more than 15 minutes. In the case of the alkaline tellurites, on account of the oxidation of these salts on heating in the air, it was also deemed advisable to weigh the water directly, after first absorbing in sulphuric acid.

The tellurium and basic element were then separated by one of the following general methods :—(1) Volatilisation of the tellurium oxide in a stream of hydrochloric acid gas. This method was used by Hutchins in the analysis of a number of tellurates (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1157). (2) Precipitation of the tellurium in presence of the other metal, by means of sulphur dioxide and hydrazine hydrochloride, and the subsequent determination of the base in the filtrate by one of the usual methods (Lenher and Homberger, *Ibid.*, 1908, xxx., 387).

The first of these methods is not applicable to the tellurites of those metals whose chlorides are sensibly volatile. It was used in the analysis of the potassium, sodium, silver, and lead salts. A weighed amount of the substance to be analysed was placed in a porcelain boat and heated in a combustion tube in a current of hydrochloric acid gas. That part of the tube which contained the boat was surrounded by a sheet-iron jacket, leaving an air space of about one inch between the jacket and the glass tube. The object of this arrangement was to make the heating more uniform. The tellurium was volatilised as $TeO_2.2HCl$. The greater portion of the tellurium was condensed in the cooler part of the tube. The excess of hydrochloric acid together with a little tellurium was absorbed in water.

The chloride remaining in the boat was weighed and calculated as metal. The tellurium sublimate in the glass tube was washed into a beaker, and the solution from the wash-bottle was added. After concentrating this solution, the tellurium was precipitated by means of sulphur dioxide and hydrazine hydrochloride.

Potassium Tellurite.—The normal salt was prepared by fusing in a platinum crucible a mixture of equimolecular quantities of potassium carbonate and tellurium dioxide. The mixture fused quite readily, giving off carbon dioxide. In order to prevent oxidation to tellurate, the air in the crucible was displaced by a stream of carbon dioxide from a generator. On cooling, a white crystalline mass was obtained, which was deliquescent and extremely soluble in water. The aqueous solution slowly deposited tellurous acid on exposure to air, and more readily when air was bubbled through the solution. On heating, however, the precipitate again dissolved, showing that at higher temperatures tellurous acid will displace carbonic acid.

A small amount of a strong solution of this substance was allowed to evaporate in a desiccator over sulphuric acid. Another vessel containing solid potassium hydroxide was placed within the desiccator to absorb the carbon dioxide of the air. The solution did not crystallise, but on evaporation it gradually formed a thick syrup, which finally solidified. The product was a hard, transparent and homogeneous mass, having a waxy or resinous appearance without the slightest external indication of crystallisation.

Two successive portions of this material were obtained, as it solidified from solution, and were analysed, with the following results :—

Calculated for $K_2TeO_3.3H_2O$.- K, 25·43; Te, 41·44; H_2O, 17·54.
Found I.—K, 25·25; Te, 40·62; H_2O, 17·71.
Found II.—K, 25·82; Te, 40·83; H_2O, 17·09.

These results indicate that although potassium tellurite, when prepared as described, cannot be crystallised from an aqueous solution, it is nevertheless a definite compound, $K_2TeO_3.3H_2O$. This compound was also prepared by treating tellurium dioxide with a solution of caustic potash, either cold or hot. The combination seems to take place only in the proportion of $2KOH : TeO_2$, so that if we have more than this proportion of dioxide, some will remain undissolved. Tellurium dioxide dissolves in a hot solution of potassium carbonate, although not so readily as in caustic potash.

Potassium Ditellurite.—Potassium ditellurite was prepared by fusing together 1 grm.-molecule of potassium carbonate and 2 grm.-molecules of tellurium dioxide. It fuses more readily than the normal salt, and on cooling appears as a white crystalline mass.

Potassium ditellurite is insoluble in cold water. It dissolves in boiling water, but on cooling the solution decomposes, yielding the normal tellurite, which remains in solution, and the tetratellurite which is precipitated. The ditellurite decomposes slightly even at the boiling temperature, for complete solution of the substance was never obtained.

Potassium Tetratellurite.—Berzelius obtained the tetratellurite of potassium by boiling a solution of potassium carbonate with tellurium dioxide, filtering the boiling solution, and allowing to cool slowly. The tetratellurite separated out in the form of small grains attached to the walls of the vessel. During the present work the tetratellurite was prepared by the decomposition of the ditellurite with water. Finely pulverised ditellurite was boiled with water for a short time. The hot solution was quickly filtered. White shining flakes separated out as the solution cooled. The compound was analysed, and its composition found to conform to the formula $K_2Te_4O_9.4H_2O$.

Calculated—K, 9·73; Te, 63·41; H_2O, 8·95.
Found I.—K, 9·76; Te, 64·51; H_2O, 8·61.
Found II.—K, 10·00; Te, 64·20; H_2O, 8·35.

This salt when boiled with its mother-liquor dissolves, but separates again on cooling. Prolonged treatment with boiling water decomposes it, leaving tellurium dioxide as the final product. A quantity of the salt which had been washed repeatedly on the filter with boiling water left a white powder which contained 0·66 per cent water, 0·47 per cent potassium, and 78·52 per cent tellurium. It was therefore nearly 99·0 per cent tellurium dioxide. It is probable that the carbon dioxide of the air played a part in this decomposition.

Sodium Tellurites.—Normal sodium tellurite was prepared in a manner similar to that by which the corresponding potassium salt was obtained. The properties of these two salts are quite similar. Sodium tellurite is readily soluble in water. It is not deliquescent, and can be crystallised from solution in the form of broad, flat plates of hexagonal outline. It was also obtained in slender needles, grouped in radiating clusters. The evaporation of the solution was conducted in the same manner as with the potassium salt, namely, in a desiccator over sulphuric acid and solid caustic potash.

Unlike potassium tellurite, which contains three molecules of water, sodium tellurite contains five molecules of water of crystallisation, $Na_2TeO_3.5H_2O$.

Calculated—Na, 14·79; Te, 40·94; H_2O, 28·88.
Found I.—Na, 14·72; Te, 40·33; H_2O, 28·89.
Found II.—Na, 14·77; Te, 40·49; H_2O, 29·14.

An interesting, though not unusual, case of equilibrium was discovered in the system, sodium tellurite, water, and alcohol. If to a strong solution of sodium tellurite we add about twice its volume of 95 per cent alcohol, the two liquids do not mix. There is, however, a redistribution of the water between the alcohol and the tellurite. The alcoholic layer increases in volume by abstracting water from the tellurite solution, while the latter becomes more concentrated. Long standing and repeated shaking will not produce any further changes in this system. If, now, we add solid sodium tellurite, it will slowly dissolve, increasing the volume of the tellurite solution and withdrawing water from the alcoholic layer. But if we add, instead, about five volumes of absolute alcohol, the water is almost completely withdrawn from the sodium tellurite and the latter is precipitated. Potassium tellurite and alcohol behave similarly.

The sodium di- and tetratellurites are analogous to the corresponding potassium salts, both in their methods of preparation and in their properties. Both of these compounds fuse below a red heat, and on cooling form clear glasses. The ditellurite, like the corresponding potassium salt, can also be obtained crystalline by fusion. The tetratellurite, when prepared by decomposing sodium ditellurite with water, has the composition $Na_2Te_4O_9.4H_2O$.

Calculated—Na, 5·97; Te, 66·07; H_2O, 9·32.
Found I.—Na, 6·06; Te, 65·78; H_2O, 9·64.
Found II.—Na, 5·78; Te, 66·35; H_2O, 9·43.

Ammonium Tellurite.—Berzelius attempted to prepare ammonium tellurite by dissolving tellurous acid in ammonia and then adding ammonium chloride or alcohol. In both instances he obtained a flocculent precipitate, which was insoluble in water but dissolved readily in ammonia. He also obtained the same substance by warming a solution of ammonium carbonate with tellurous acid or tellurium tetrachloride, and adding ammonium chloride. On heating this compound, ammonia was evolved, and a residue of tellurium dioxide remained. The amount of this residue in one case was 83·1 per cent; in another it was 83·87 per cent, while the calculated amount of tellurium dioxide in the compound $(NH_4)_2Te_4O_9.4H_2O$ is 83·7 per cent. He therefore concluded that his precipitates were tetratellurites, exactly analogous in composition to the corresponding salts of potassium and sodium. Berzelius also evaporated to dryness, with the aid of gentle warming, a solution of tellurous acid in ammonia. He found the residue to be principally hydrated tellurium dioxide containing a little ammonia.

In the present work tellurium dioxide was dissolved in ammonium hydroxide (sp. gr. 0·91) by heating in sealed tubes for 10 hours at a temperature of 95—100°. After cooling and filtering the solution was allowed to evaporate spontaneously. As the solution evaporated, small crystals were obtained in the form of short needles arranged in radiating groups, or clusters of thin transparent plates. On drying these became opaque. They dissolved readily in ammonia, but were insoluble in water.

They were analysed as follows:—A weighed amount of the residue was placed in a porcelain boat inside of a glass combustion tube. This tube was connected to an absorption apparatus containing a standard solution of sulphuric acid. While a slow current of dry air was drawn through the tube, the boat was heated, gently at first, increasing the temperature gradually to the full heat of the Bunsen burner. A considerable amount of moisture was condensed upon the cooler part of the tube. The residue in the boat was weighed as tellurium dioxide. The excess of acid in the absorption apparatus was then titrated with standard alkali, and the amount of ammonia estimated. The water was estimated by difference.

The following composition was found:—Ammonia 1·69 per cent, tellurium dioxide 89·19 per cent, and water 9·12 per cent. This would correspond to the formula $NH_3.5TeO_2.5H_2O$ or $5H_2TeO_3.NH_3$. It is not believed that this is a definite compound. It is more likely that this is but one stage in the decomposition of ammonium tellurite to hydrated tellurium dioxide. The crystals obtained from the ammoniacal solution were probably a definite ammonium tellurite. This compound, however, is so unstable that it can exist only in solution, or when surrounded by the mother-liquor, and when dried it spontaneously decomposes, even at the ordinary temperature.

(To be continued).

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

(Concluded from p. 183).

(c) *Procedure and Notes. Procedure* II.—The group precipitate (P. 1) which consists of ZnS, MnS, CoS, and NiS is transferred to a casserole and treated with 10—20 cc. of HCl (1 : 12). Stir the mixture thoroughly for 2—3 minutes; if a black residue remains the presence of Ni and Co are indicated and a few crystals of $KClO_3$ should be added. Boil the mixture for a few minutes, dilute with a little water, and filter off the yellow residue of sulphur. Evaporate the filtrate to a few cc. to remove excess of acid; add 10—20 cc. of water and make slightly alkaline with 5N NaOH. If the precipitate which forms is so large that the mixture becomes gelatinous, add 10—20 cc. of water, cool the mixture and add solid Na_2O_2 in very *small* portions until a steady evolution of gas continues after the mixture has been well stirred. Heat to incipient boiling and filter (Precipitate, P. 4; Filtrate, P. 3).

Notes.

(1) The MnS and ZnS usually dissolve readily in cold HCl (1·12); the NiS and CoS are quite soluble in concentrated HCl but dissolve very slowly (see T. E., Series III.). If a black residue remains after the treatment with HCl the presence of Co and Ni is indicated. The absence of a black residue does not prove, however, that Ni and Co are not present in the precipitate.

All the sulphides of this group are readily soluble in HCl (1·12) and $KClO_3$. The group precipitate is first treated with HCl in order to obtain indications as to the presence of Ni and Co. HCl and $KClO_3$ are used to dissolve the precipitate in preference to *aqua regia*, since much free sulphur is formed at the start if the latter is used.

(2) NaOH completely precipitates Mn and Ni as $Mn(OH)_2$ and $Ni(OH_2)$; these substances do not dissolve in a moderate excess of this reagent. The $Zn(OH)_2$ dissolves readily, however, in an excess because it is an amphoteric substance. The product of the reaction is sodium zincate, $Na_2Zn_2O_2$ (see T. E., Series VI.). If an excess of NaOH be added to $Co(OH)_2$ a portion, of the latter dissolves forming a blue solution, the colour of which is due, probably, to Na_2CoO_2. Therefore, great care must be exercised to avoid an excess until the cobalt is oxidised to the "-ic" condition.

The Na_2O_2 converts the $Zn(OH)_2$ into soluble Na_2ZnO_2, $Mn(OH)_2$ into a brown $MnO(OH)_2$, $Ni(OH)_2$ into black $Ni(OH)_3$, and $Co(OH)_2$ into black $Co(OH)_3$.

(3) The Na_2O_2 is added to a cold solution, as it decomposes with explosive violence when the solution is hot. Oxygen is liberated during the decomposition. Boiling decomposes excess of sodium peroxide.

(4) The separation of zinc by this method is very satisfactory. When the directions have been followed care-

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fully the filtrate is free from Ni and Co, which usually interfere with the later tests for Zn.

Procedure III.—The filtrate obtained from P. 2 contains sodium zincate. Acidify the solution with acetic acid, $HC_2H_2O_2$, warm to about 70°, and saturate with H_2S. A white, flocculent precipitate, ZnS, confirms the presence of Zn. If results are doubtful, the confirmatory tests may be continued as follows:—Filter, wash the precipitate of ZnS, then dissolve it in the least amount of HNO_3. Evaporate nearly to dryness to expel excess of acid, neutralise with a few cc. of Na_2CO_3 solution. Add a volume of $Co(NO_3)_2$ equal to that of one-sixth the solution in the casserole, evaporate to dryness and ignite gently. A green residue, ZnO.CoO, or $CoZnO_2$, confirms Zn.

Notes.

(1) Zn is precipitated readily from warm dilute $HC_2H_3O_2$. If but fractions of a mgrm. are present the precipitate coagulates slowly; therefore care must be exercised or the precipitate will be missed.

(2) If a white flocculent precipitate forms at once when the $HC_2H_3O_2$ solution is treated with H_2S, a confirmatory test is unnecessary as the action is highly characteristic of Zn. Mn is the only other element of the group which forms a light coloured sulphide and it is not precipitated in the presence of acetic acid.

(3) The composition of the green salt obtained in the confirmatory test for Zn is probably represented by the formula $CoZnO_2$. A large excess of Co salt should be avoided, as the black colour of CoO obscures the green colour.

Procedure IV.—The Na_2O_2 precipitate (P. 2) which contains $MnO(OH)_2$, $Ni(OH)_2$, and $Co(OH)_3$ should be washed thoroughly to insure the removal of the soluble adhering zinc salt, then transferred to a casserole and dissolved in the least quantity of warm HCl (1 : 12). Filter to remove paper and evaporate filtrate to about 2 cc. Add 5 cc. of HNO_3 (1 : 20), boil until the reddish brown fumes cease to be given off, then add 10—20 cc. of HNO_3 (1·20), heat to boiling and add several crystals of $KClO_3$, continue to boil gently for several minutes. Cool the mixture and allow any suspended matter (probably a precipitate of MnO_2, if it has a brown colour) to settle. Decant the liquid through an asbestos filter in such a manner that most of the precipitate (if there is one) remains in the casserole. Test the filtrate by boiling it with a crystal of $KClO_3$. Filter if more precipitate forms (Precipitate, P. 5; Filtrate, P. 6).

Notes.

(1) Manganous salts of the type of $MnCl_2$ are rapidly oxidised to MnO_2 by $KClO_3$ in the presence of HNO_3 (see T. E., Series VIII.). As MnO_2 is readily soluble in the presence of reducing agents all fragments of filter paper must be removed from the HNO_3 solution. The HCl must be removed previously by evaporation, since it reacts with HNO_3 to form oxides of nitrogen in which MnO_2 is readily soluble. The separation of manganese by this method is very satisfactory; small fractions of a milligrm. of the metal are easily detected.

(2) The MnO_2 is filtered off by means of an asbestos filter. This filter is easily prepared by placing a small loose plug of glass-wool well down in the apex of the ordinary glass funnel, and spreading a large layer of asbestos over it. If filtration is slow, suction may be used.

Students in this laboratory have experienced no trouble whatever in executing the various steps described in this procedure.

Procedure V.—Place the $HClO_3$ precipitate (P. 4) in a casserole, add 20 cc. of HNO_3 (1 : 40), boil for a few minutes, add 1 grm. of PbO_2, and boil again for 2—3 minutes. Pour the mixture into a test-tube, and allow any suspended matter to settle. A pink or violet coloured solution confirms manganese.

Notes.

(1) When Mn is precipitated as MnO_2 by $KClO_3$ in HNO_3 solution, the confirmatory tests are really superfluous, as this reaction is highly characteristic of Mn.

Procedure VI.—Evaporate the filtrate from the $HClO_3$ treatment (P. 4) to about 5 cc. to expel excess of acid, add 10—15 cc. of water, filter, if turbid, then add NaOH solution, drop by drop, until the solution is neutral, or until a permanent precipitate begins to form. Divide the mixture into two equal parts. Test one for Co by Procedure VII., and the other for Ni by Procedure VIII.

Procedure VII.—Add $HC_2H_3O_2$ to one-half the neutral solution obtained in P. 6 until it is barely acid in reaction, then add an equal volume of a saturated solution of KNO_3. Warm the mixture, and allow to stand for an hour if a precipitate does not form sooner. A yellow pulverulent precipitate, $K_3Co(NO_2)_3$, indicates Co. Filter, wash the precipitate with KNO_2 solution, and test it with a borax bead. A blue colour confirms Co.

Notes.

(1) The yellow pulverulent precipitate, potassium cobaltic nitrite, $K_3Co(NO_2)_6$, forms slowly. Therefore it is advisable to allow the precipitate to stand for an hour. However, distinct tests are obtained in twenty minutes when 0·0003 grm. of Co are present, although precipitation is not complete after four hours. The yellow precipitate is slightly soluble in water, but not in a strong solution of KNO_2, owing to the presence of the common ion, K+.

(2) The theory of the formation of the salt is indicated by the following equations:—

$$+NO_2^- + H^+ C_2H_3O_2^- \rightleftharpoons H^+ NO_2^- + K^+ C_2H_3O_2^+,$$

$$Co^{++}(C_2H_3O_2^-)_2 + 2K^+ NO_2^- \rightleftharpoons Co^{++}(NO_2^-)_2 + 2K^+ C_2H_3O_2^-,$$

$$Co^{++}(NO_2^-)_2 + 2H^+ NO_2^- \rightleftharpoons Co^{+++}(NO_2^-)_3 + H_2O + NO,$$

$$Co^{+++}(NO_2^- \quad + NO_2^- \longrightarrow K_3Co(NO_2)_6.$$

(3) Nickelous salts are not oxidised by nitrous acid, HNO_2, and are not precipitated by KNO_2, except in very concentrated solutions. By diluting the solutions as directed the precipitation of Ni is avoided. Potassium nickelous nitrite, $K_4Ni(NO_2)_6$, is dark yellow to red in colour. (See Lang, *Journ. Prakt. Chem.*, 1862, lxxxvi., 299; Hampe, *Ann.*, 1863, cxxv., 346; and Richards, *Chem. Ztg.*, 1904, xxviii., pp. 479, 885, 912).

Procedure VIII.—Add KCN to the other portion of the neutral solution (P. 6) until the precipitated cyanides just re-dissolve. Heat the solution (do not boil) with frequent stirring for two or three minutes. Filter off any residue that may be present. Add a relatively large amount of NaOH solution, then bromine water until the reddish brown colour of the bromine water persists. A black precipitate, $Ni(OH)_3$, indicates Ni. The borax bead test may be used to confirm Ni.

Notes.

(1) The addition of KCN to the neutral solution containing Ni and Co salts results in the precipitation of green $Ni(CN)_2$ and brown $Co(CN)_2$. These cyanides dissolve readily in excess of KCN, forming the soluble complex cyanides $K_2Ni(CN)_4$ and $K_4Co(CN)_6$. The cobalt salt readily undergoes oxidation when in the presence of air, and tends to pass from the cobalto cyanide to the cobalti-cyanide, thus:—

$$2K_4 + [Co(CN)_6]^{=} + O + H_2O \rightleftharpoons 2K_3 + [Co(CN)_6]^{\equiv} + 2K + OH^-.$$

The complex nickel salt is more stable in the air, and moreover forms no compound corresponding to the cobalticyanide. However, in the presence of strong oxidising agents like chlorine, bromine, or the hypochlorites in alkaline solution, the complex nickelous salt is oxidised to

the nickelic state, in the form of a simple salt, which is then precipitated as black $Ni(OH)_3$. The final results of the reaction may be formulated as follows :—

$$2K_2Ni(CN)_4 + NaClO + 5H_2O \rightarrow 2Ni(OH)_3 + NaCl + 4KCN + 4HCN.$$

Hence, under the same oxidising treatment the potassium cobalto-cyanide is converted into the soluble potassium cobalti-cyanide, while the potassium nickelous-cyanide is converted into the insoluble $Ni(OH)_3$, and may be separated by filtration.

The cobalt is not precipitated, probably because the complex ion $[Co(CN)_6^{=}$ is so slightly dissociated into Co^{+++} and CN^{-} ions.

Summary.

(1) Attention has been directed again to the well-known fact that the methods which are generally used in qualitative chemical analysis have received but little systematic study and are in need of revision.

(2) A comparison of a large number of methods for the precipitation and analysis of the Zinc Group as outlined by the respective authors has been made, and the inaccuracies and discrepancies of the procedures noted.

(3) A method has been formulated by which the difficulties usually encountered in attempting the complete precipitation of zinc, manganese, nickel, and cobalt have been overcome without introducing intricate procedures. By a series of test experiments it has been shown that a quantity as small as 0·0005 grm. of any one of the metals in the presence of large amounts of any or all of the other metals may be readily detected.

(4) In the second part of the paper, which relates to the subsequent analysis of the group precipitate, it has been shown that the usual methods of procedure are entirely inadequate for making an accurate analysis, and that the methods proposed in this paper are adequate for confirming even 0·0005 grm. of any of the metals of the group.

(5) The accuracy and general utility of the proposed methods have been proven, as shown by Series XII. of the Test Experiments.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Mediæval Science.

M. Pierre Duhem, who has just finished a third volume consecrated to Leonardi da Vinci, has attempted to rehabilitate the scholars of the Middle Ages. It is believed in a general way that the discoveries of the celebrated painter, who was at the same time a great engineer and a great philosopher, owed nothing to mediæval science. In a letter addressed to the Academy, M. Duhem complains that "the scholars of the Renaissance are always placed in opposition to Aristotle, as if human thought had absolutely come to a standstill during the Middle Ages." Now such is not the case. According to the researches of M. Duhem, it seems that the scholars of Paris had already, in the fourteenth century, founded a dynamic which is not opposed to the one of which Leonardi da Vinci established the principles in the beginning of the sixteenth century. Albert de Saxe, Buridan, Nicolas, Oresne were precursors of Leonardi da Vinci.

Two Comets Visible in the Sky.

The hazy sky of the last few days has prevented the astronomers of the Paris Observatory from observing a new comet, the *Westphal* Comet that was lately discovered in Piata on September 26 last. Its brilliancy, which is at present weak, will very probably increase next month. At present this comet of the seventh or eighth magnitude is not visible to the naked eye. But a simple spy-glass is sufficient to enable one to see this star, the nucleus of which is nebulous and the coma round, and is now shining in the constellation of Versean. From recent observations this comet has been identified with a comet that had not been seen since 1852. It is, then, a new periodical comet that has just been discovered in the heavens, the period of which appears to be of sixty-one years. The number of periodical comets not being very high—not more than a score—this astronomical discovery is important. Since the beginning of the present year four new comets have been signalled by the observatories of the different countries. The comet 1913 *b*, whose spectrum has just been studied by M. Bosler at the Meudon Observatory, is the Metcalf Comet. In a note presented before the Academy of Sciences by M. Deslandres, M. Bosler indicates the presence of hydrocarbons and cyanogen in the atmosphere which is the normal compositlon of comets.

The Committee of Enquiry on the Metre.

The members of the International Committee of the Metre, which met on October 10 at the Ministry of Commerce to register recent progress of the metrical system, and to study the improvements yet to be brought to bear upon it, were present at the sitting of the Academy of Sciences. M. Derboux, perpetual secretary, welcomed MM. Foerster, chairman, Blaserna, secretary, Egorof, delegate from Russia, Gautier, director of the Observatory of Geneva, von Lang, member of the Academy of Science of Vienna, Tanakadate, of the University of Tokio, who were seated in the space reserved for the members of the Paris Institute. In presenting the reprint of the official reports of the Academy of Sciences from 1808 to 1811, M. Darboux recalled to mind the fact that one of the first decennial prizes founded by Napoleon I. was awarded to the authors of the studies that served as the basis of the metrical system.

Cochineal Devours certain Noxious Insects.

Some years ago the orange trees and lemon trees of California were ravaged by an insect, to which entomologists have given the barbarous name of *Iceria purchasi*. A learned American discovered an Australian cochineal, *Novius cardinalis*, which had been created by Nature on purpose to devour these devastating insects. Mr. Riley brought some of these cochineals from Australia, and in less than a month they reduced the *Iceria* to infinitesimal and insignificant numbers. These insects appeared in Portugal and in Italy in 1910. The French coast had remained unmolested. But in the month of May, 1912, the owner of a garden situated in the peninsula of Cape Ferrot in the department of the Alpes Maritimes sent to the Minister of Agriculture an unknown insect which was immediately recognised as the terrible *purchasi*. M. Marchal, Member of the Academy of Sciences, who relates this interesting story, had eight cochineals sent from Portugal and from the Portici Laboratory in Italy. One month after numerous descendants of these *Novius* were sent to the gardens of Cape Ferrot. Squads of a hundred cochineals were deposited on the attacked orange trees and lemon trees. In June and July last one could almost think that the noxious insects had been completely eradicated ; but M. Marchal has noticed, however, that whole colonies of these insects yet remain. But the cochineals chase them unceasingly, and in the end the victory must be theirs.

Wireless Telegraphy Signals.

A new crystal detector, into which two physicists, MM. Dongier and Brazier, have passed an alternating current, has enabled these *savants* to make Hertzian waves, sent by the Eiffel Tower, to be heard in specially satisfactory conditions. At the Paris Observatory, by the help of an antenna only 30 metres high, MM. Dongier and Brazier, by uniting the detector to a phonographic pavilion, have been able to hear the crackling of tbe long or short sparks of the wireless telegraphy at 20 metres from the acoustic trumpet. It is Prof. Bouty who communicated the notice

of the two physicists to the Academy of Sciences. If the ear is placed at the entrance of the acoustic trumpet, the antenna may be reduced to 3 metres in height.

A New "Curie."

The last International Congress of Radio-activity which was held in London in March, 1912, defined the unity of radio-activity to which has been given the name "Curie," in remembrance of the marvellous discovery of radium by M. and Mdme. Curie. This unity corresponds to the state of equilibrum of a grm. of pure radium with two-thirds of a cubic milimetre of emanation. This state of equilibrium indicates that in these particular conditions radium does not give off any more enanation. But the Curie could hardly be employed practically, this unit of measurement being much too large. A physicist, M. Marckwald, has just proposed a new definition of the Curie. He has noticed, after numerous experiments, that in the most varied pitchblendes the relation of pure radium to uranium was a constant, equal on an average to three 10-millionths. To this constant the Professor wishes to give the name of Curie. In the pitchblendes the amount of uranium varies from one to eight, the richest in uranium being the pitchblendes of Western Africa; but, however, the relation of radium to uranium remains invariable. It is highly probable that the new Curie, the application of which may be important in the study of the physics of the globe, of the radio-activity of thermal waters, &c., will be adopted by the next International Congress.

A New Mountain Observatory.

France has lately become possessed of a new Mountain Observatory. Two engineers of Geneva, MM. Honegger and Amiet, have, indeed, just established an observatory destined for the study of physical astronomy of spectrography and meteorology at Saleve, in the Haute-Savoie. This mountain, whose altitude is 1365 metres, generally rises above the mists and fogs that hide the sky of Geneva during the winter nights. Thus numerous observations may be made in satisfactory atmospheric conditions, with the help of a large telescope with an aperture of one metre in diameter, that has been installed on Mount Saleve by M. Schaer, an astronomer of the Observatory of Geneva. The high mountain meteorological observatories are four in number. They are the observatories of the Puy de Dôme, at an altitude of 1460 metres; of the Pic du Midi at 2850 metres; of the Mount Ventoux in the department of Vaucluse at 1900 metres; and lastly that of the Aigonal, formed by a forestry station of the Cevennes at 1550 metres, near the little village of Valleraugue. Two meteorological stations of less importance are to be found; one on Mount Monnier at 2740 metres above Nice; the other on the Ballon de Servance, in the Vosges mountains, at a height of 1200 metres. From each of these six stations, now increased to seven by the creation of the observatory of Saleve, meteorological despatches are sent every day to the central bureau of Paris. As to the astronomical observatories, France possesses eight, without counting those of Algiers and the Saleve. These observatories are situated at Paris, Meudon, Bescançon, Saint-Genis-Laval near Lyons, Marseilles, Nice, Toulouse, and Floirac, near Bordeaux.

A New Parachute.

A new aviator's parachute has just been invented by an officer attached to the aeronautic service at Vincennes, Captain Couade of the Engineers. The delicate point of these parachutes consists, as is well known, in the manner of assuring the development of the parachute, at the right moment, without any possible mishap. M. Lecorum, who has presented Captain Couade's notice to the Academy of Sciences, showed that the problem had been solved very ingeniously by means of a little auxiliary parachute, which, placed at the back of the aeroplane, is joined to the large parachute by a direct machinery. A simple manœuvre can unfasten the little parachute, which, under the influence of the speed of the aeroplane, draws back the large parachute and causes its development. The resistance of the large parachute is so great that the aeroplane upheld descends gently and vertically to earth. To avoid any sudden movements a brake regulates the manœuvre of the development of the little auxiliary parachute.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 4, July 28, 1913.

Sulphur Liberated by the Action of Water on Sulphurous Acid.—E. Jungfleisch and L. Brunel.—The sulphur set free by the decomposition of sulphurous acid is soft sulphur, but its state is dependent upon the temperature at which the separation occurs. Above 113°, the melting-point of octahedral sulphur, it is fused to a liquid which on cooling crystallises in a form which differs according to the temperature. If the mixture is kept below 100° the sulphur still fuses, and after fusion is precipitated in crystalline masses or in liquid droplets which finally crystallise. At 68–70° it separates in the form of very minute spherical globules, which form agglomerations when heated. In this state the substance has the characteristic properties of soft sulphur. When the reaction between sulphurous acid and water takes place at the ordinary temperature it occurs very slowly, and the sulphur formed is crystalline.

Negative Photocatalysis of Hydrogen Peroxide.—Victor Henri and René Wurmser.—When traces of various substances, *e.g.*, soda, iodine, are added to hydrogen peroxide it becomes stable towards the ultra-violet rays. It is possible that in many cases of catalysis by ferments or colloidal metals the poisons or antiferments act upon the substance undergoing transformation, and not upon the diastase or catalyst. There is a very close relation between the action of certain ferments and that of the ultra-violet rays.

Quantitative Separation of Chromium and Aluminium. Analysis of Chromite.—F. Bourion and A. Deshayes.—The separation of chromium and aluminium can be effected by subjecting them to the action of a mixture of chlorine and sulphur dichloride, which gives satisfactory results, provided that ammonium sulphate is added to the mixed oxides if more than 20 per cent of chromic oxide is present. With mixtures containing less than 50 per cent of chromic oxide there is always a small residue which is not attacked. In order to bring about the complete chlorination of chromite the mineral must previously be heated to a red heat with mercuric sulphate. After chlorination the constituents of the mixture can be separated into three groups:— (i.) The non-volatile chlorides of magnesium and calcium; (ii.) the volatile chloride of chromium which is insoluble in water; (iii.) the volatile chlorides of iron and aluminium which are very soluble in water. This method of analysing chromite is very rapid, but the silica (which remains with the non-volatile chlorides) cannot be estimated by means of it.

No. 5, August 4, 1913.

Absorption of Ultra-violet Rays by Mineral Dyes in Aqueous Solution.—MM. Massol and Faucon.—Different mineral colouring matters, *e.g.*, potassium ferrocyanide, copper sulphate, potassium chromate, absorb the invisible ultra-violet rays unequally. The absorbent action of synthetic organic dyes is much greater than that of the mineral dyes, but it is of the same order qualitatively, and broad absorption bands, if they exist, are found in the same regions of the spectrum.

Rôle of Uranium Salts as Photochemical Catalysts.—Daniel Berthelot and Henry Gaudechon.—No fluorescent or radio-active substances which the authors have examined accelerate photochemical reactions, with the exception of uranium salts. The action of the uranium salts is limited to a special class of reactions, namely, the decomposition of linear acids, particularly if they are dibasic or complex. These reactions occur spontaneously in ultra-violet light, but the photocatalyst makes them take place in visible light; thus it lowers the vibratory frequency of the photochemical reaction in the same way as an ordinary catalyst lowers the temperature of a chemical reaction.

Products of Incomplete Reduction of Ceric Oxide.—A. Damiens.—In 1902 Sterba described a new compound which he called cerium oxycarbide, $CeC_2.2CeO_2$. He obtained it by the action of a limited quantity of carbon upon ceric oxide, in Moissan's electric furnace. The investigation of the process, however, appears to show that the product is really a mixture of cerium oxide and carbide. The reduction of ceric oxide by carbon apparently takes place in three stages: — $2CeO_2 + C = Ce_2O_3 + CO$. $Ce_2O_3 + 9C = 2CeC_3 + 3CO$. $CeC_3 = CeC_2 + C$.

No. 6, August 11, 1913.

Quantitative Study of the Absorption of Ultra-violet Rays by Acids of the Ethylenic Series.—Jean Bielecki and Victor Henri.—The ethylene bond increases the absorption power for ultra violet rays in the ethylenic acids the increase being greater the nearer the double bond is to the carboxyl group. The geometrical isomers, fumaric and maleic acids, and mesaconic and citraconic acids, have different powers of absorption, the *cis* form absorbing less than the *trans* form. From the authors' results the following general law can be enunciated:—With a substance of formula A B C the constant of molecular absorption E is equal to a product $a\,b\,c\,\ldots\,\alpha\,\beta\,\ldots$ in which a, b, c are factors corresponding to the different molecular groups A, B, C, and α, β . . . are factors which indicate the bonds, configurations, and reciprocal positions of these groups.

Molecular Weight of Sulphuric Anhydride.—H. Giran.—The author has determined the heat of vaporisation L of liquid SO_3, and also the heat of solidification S. Then applying de Forcrand's formula, $\frac{L+S}{T}$ = molecular weight, he concludes that the simple formula SO_3 represents the molecule of the gaseous anhydride at the moment of vaporisation.

γ-Phenyl-oxycrotonic Acid.—J. Bougault.—The more detailed study of the behaviour of γ-phenyl-oxycrotonic acid shows that the formula $C_6H_5.CHOH.CH=CH.CO_2H$ agrees best with its chief reactions, although the evidence in its favour is not absolutely decisive. It is noticeable that the transformation of α-phenyloxycrotonic acid into γ-phenyloxcrotonic acid is limited by the inverse reaction and is reversible.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 11, 1913.

Preparation of Hexamethylbenzene. — Hans Reckleben and Johannes Scheiber.—When an equimolecular mixture of the vapour of methyl alcohol and acetone is led over heated aluminium oxide large quantities of hexamethylbenzene are obtained. Probably mesitylene is first formed and reacts with the methyl alcohol under the influence of the catalyst. Aromatic hydrocarbons can be methylated in presence of aluminium oxide by the action of methyl alcohol, but the acetone-methyl alcohol mixture gives better yields. Hexamethylbenzene can easily be brominated, but the authors have not ascertained for certain whether the product is the hexabromide.

Action of Methyl Magnesium Iodide on Silicon Hexachloride.—Geoffrey Martin.—If a molecule of methyl magnesium iodide is allowed to act on one molecule of silicon hexachloride in ethereal solution no volatile methyl derivative of Si_2Cl_6 is obtained, but a yellow powder which is insoluble in acids and in organic solvents separates. Its composition is represented by the formula $CH_3.Si_6O_{13}H_9$. One grm. of it when treated with potash solution yields 169 cc. of hydrogen, and probably the molecule contains three pairs of silicon atoms directly united with one another. When the substance is heated to temperatures of from 200°—400° it gives a mixture of hydrogen and methane, yielding finally a silicon compound which contains no carbon.

Autoxidation of Chromous Salts.—Jean Piccard.—In neutral or acid solution chromous salts on autoxidation yield chromic acid as well as chromic salts. Intermediate products of great oxidising power are formed, and are stable for an appreciable time. They can be titrated separately and comprise two oxides, one of which is very unstable while the other is rather more stable. The existence of another oxide, which is not stable for an appreciable time, must be assumed. No formulæ can as yet be definitely ascribed to these oxides, but the first is probably O:Cr.O.O.Cr:O.

MISCELLANEOUS.

Change of Address.—Messrs. Haseltine, Lake, and Co., Patent Agents, announce that their present address is 28, Southampton Buildings, Chancery Lane, W.C., having removed from 7 and 8, Southampton Buildings.

The Chemical Society of the University of Liverpool.—This Society, which celebrates its twenty-first anniversary this session, will hold its Annual Dinner on Saturday, November 29, at the Midland Adelphi Hotel, Liverpool. Full particulars can be obtained from W. M. INMAN, Hon. Sec., University, Liverpool.

Faraday Society.—A General Discussion on "The Passivity of Metals" will take place on Wednesday, November 12 next, in the rooms of the Chemical Society, Burlington House, London, W. The meeting will be open to Fellows of the Chemical Society, Members of the Society of Chemical Industry, the Iron and Steel Institute, the Physical Society of London, and the Institute of Metals. Others interested in the subject desirous of being present should apply to the Secretary of the Faraday Society. The President-elect, Sir Robert Hadfield, F.R.S., will preside, and the following provisional programme has been arranged:—Dr. G. Senter will open the Discussion with a general Introduction to the subject; Dr. G. Grube (Dresden) will read a paper on "Some Anodic and Cathodic Retardation Phenomena and their Bearing upon the Theory of Passivity"; Dr. D. Reichinstein (Zürich) will read a paper on "Interpretation of Recent Experiments Bearing on the Problem of the Passivity of Metals"; Mr. H. S. Allen will read a paper on "Photo-electric Activity of Active and Passive Irons." Communications will be read from Prof. Dr. G. Schmidt (Münster); Prof. Dr. Max LeBlanc (Dresden); Prof. Dr. E. Schoch (Texas); Prof. Dr. Günther Schulze (Reichsanrtalt Charlottenburg). The meeting will then be open for general diacussion. Sir Robert Hadfield, Dr, J. Newton Friend, Mr. R. N. Lennox, and others will show specimens of non-corrodible metals and alloys. Members desirous of contributing papers to the Discussion or exhibiting any specimens are requested to communicate at once with the Secretary.

MEETINGS FOR THE WEEK.

THURSDAY, 30th.—Chadwick Public Lectures, 5. (The University, Bristol). "Physiological Principles of Heating and Ventilating," by Dr. Leonard Hill.

ERRATUM.—P. 188, col. 2, line 3, *for* "irregularities" *read* "regularities."

THE CHEMICAL NEWS

Vol. CVIII., No. 2814.

NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

(Concluded from p. 204).

IV. *Swelling up of Liquid Crystals and Myelin Forms.*

If water is continually added to anhydrous neutral ammonium oleate the crystals of this salt disappear, and more and more crystals of the liquid-crystalline neutral ammonium oleate appear until finally they only are present, as has already been shown. At this stage the quantity of water added is just sufficient to convert the anhydrous into the hydrated oleate, and the amount of water contained in the latter can be accurately expressed in numbers, if the mixing is performed on the balance and the result is continually tested by the microscopic examination of small specimens. If the liquid-crystalline hydrate of ammonium oleate thus obtained is placed on a glass plate and rubbed up with more water by means of a spatulum, it is found that (until certain limits are reached) these further quantities of water are completely taken up by the substance. The latter does not change into a paste of liquid crystals and water, *i.e.*, into a heterogeneous mass, but it remains homogeneous, takes up a larger volume and swells up, finally being converted into a more sticky substance, the double refraction of which is smaller for equal thickness (Note 8). In order to prevent the hydrolytic decomposition of the oleate it is better to use ammonia instead of water. The dissolved ammonia has a protective action without having any ill effect, since there is no basic ammonium oleate, so that the ammonia is not taken up by the mass.

Swelling up is generally a process of a chemical nature. Thus the anhydride of calcium sulphate swells up in damp air, forming gypsum, *i.e.*, hydrated calcium sulphate. A solution of the anhydride in water is first formed, and since it is saturated with gypsum the latter crystallises out, then a corresponding fresh quantity of anhydride dissolves, and this process is continued until finally all the anhydride is converted into gypsum. In aqueous solution the swelling up is not seen, because the gypsum dissolves too readily in water. The fact that it can be observed in the case of ammonium oleate is due to the insolubility of the hydrated product resulting from the swelling. It can remain for a long time in contact with a large excess of water, but it gradually forms a colloidal solution (soap water) (see F. Goldschmidt and L. Weissman, *Kolloid-Zeit.*, 1913, xii., 18), the dissolved substance breaking up to form small solid particles in suspension, which can no longer be detected by ordinary microscopical methods. Probably a hydrate with a still larger percentage of water is formed. By the addition of salt (ammonium chloride or bromide, &c.) the process is reversed and a liquid solution, rich in water, is formed, while if no such addition is made the process is irreversible.

R. Virchow was the first to observe these swelling up phenomena in the investigation of animal tissues and parts of the nerve substances (*Arch. Path. Anat.*, 1853, vi., 562, "On the Wide Distribution of a Substance Analogous to Nerve Marrow in Animal Tissues." He compares the process to that occurring when starch is put into warm water; see also O. Lehmann, "Molecularphysik," 1888, i., 546, Sect. 3 and 4). Virchow was of the opinion that they are the characteristic peculiarity of a definite substance formed in the organism, which he called myelin. He did not attempt to find a physical explanation of the peculiar thread and drop-shaped forms resulting from the process; they appeared to him to be a phenomenon necessarily accompanying the swelling up process, and of secondary importance.

F. W. Beneke ("Studien über das Vorkommen, die Verbreitung und die Funktion von Gallenbestandteilen in den thierischen und pflanzlichen Organismen," Giessen, 1862) succeeded in obtaining similar formations by introducing crystals of cholesterin into soap water, and also by adding to pure water the residue obtained by the evaporation of the alcoholic extract of boiled yolk of egg, as Goblez had already observed (after Virchow).

C. Neubauer (*loc. cit.*, 1866, xxxvi., 303) then showed that a definite substance, "myelin," of which these swelling up phenomena were characteristic, does not exist, and that the same "myelin forms" are obtained when pure oleic acid and aqueous ammonia are brought together. Since the latter combines with the oleic acid to form neutral ammonium oleate hydrate, he might have further concluded that this hydrate must give myelin forms when brought into contact with ammonia. He did not make this inference, and the mention of the use of oleic acid led G. Quincke to put forward his theory, recently revived by A. Mlodziejowski (neglecting the fact that the acid is decomposed by ammonia), that the myelin forms consisted of a thick paste of solid ammonium oleate crystals in an envelope of oleic acid, a theory which was proved to be untenable (G. Quincke, *Wied. Ann.*, 1894, liii., 603; see also J. Gad, *Archiv. Phys.*, 1878, p. 181; G. Quincke, *Archiv. Phys.*, 1879, xix., 129; E. Brücke, *Wien. Sitzungsber.*, 1879, iii., 79, 267; Famintzin, *Bull. Acad. St. Petersb.*, 1884, xxix., 414; O. Lehmann, "Molekularphysik, 1888, i., 523). He gives the following summary of it:—"The oleic acid with much alkali and a little water forms at the surface of contact with freshly introduced water thin layers of oleic acid, which rapidly surround either the remaining soap crystals or those freshly formed (neutral or acid alkali salt of oleic acid with water of crystallisation), and form the myelin structures. These myelin forms alter, the liquid oleic acid skin giving up water to the soap crystals. The volume of these soap crystals, which gradually alter and break up, is thus increased. The resulting soap solution periodically exceeds the limits of the oleic acid, and aqueous liquid produces eddies and peculiar movements. This spreading out and the flowing of the liquid may draw out the hollow envelopes of oleic acid filled with soap crystals to form long hollow threads of oleic acid, filled with sticky masses or soap crystals. In consequence of the surface tension at the bounding surface of the oleic acid and surrounding liquid these threads of oleic acid collect together and form hollow balls or bubbles. These hollow bubbles filled with aqueous soap solution or sticky masses of soap are displaced by the periodic spreading out of the soap solution at the surface of the skin of oleic acid, both in the surrounding aqueous liquid and also along the hollow threads of oleic acid, and run together to form one or more larger hollow balls or bubbles." I was at first misled by these statements, because I thought I had observed phenomena which confirmed them. In particular I thought I could demonstrate the existence of a skin of oleic acid and of differences of surface tension which might cause the formation of the peculiar forms, although I had already realised that it was not a question of solid but only of liquid (or, at any rate, fluid) ammonium oleate crystals. From my continued experiments (with other substances also) I gradually came to the conclusion that Quincke's theory is untenable, is due to different optical illusions, and gives no explanation of the phenomena (*Wied. Ann.*, 1895, lvi., 771; *Ann. Phys.*, xix., 22, 407; 1906, xx., 63; "Die scheinbar lebenden Kristalle," Esslingen, 1907; *Biolog. Zentralbl.*, 1908, p. 481; "Die neue Welt der flüssigen Kristalle," 1911, p. 264). The hypothetical oleic acid envelope of the myelin forms does not exist, and thus there is no question of differences of surface tension. The myelin forms are only

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

liquid crystals of peculiar molecular structure. Their surface tension is the same at all places, and their formation is due to the action of the same shaping force which, in conjunction with alterations of surface tension owing to swelling up, determines the shape of liquid crystals (Note 9). In any case it cannot be directly deduced from the known facts that we are dealing with forces which are not known in Physics, and the study of which will probably explain many actions which cannot be understood from a physical point of view, but which come into play in the organic kingdom; for the myelin forms and the apparently living crystals allied to them are the only lifeless structures which exhibit close analogies to the organism, which consists of the same molecules as lifeless substances.

The normal liquid crystals of neutral ammonium oleate hydrate are converted continuously into the myelin forms, although the water is taken up only in stochiometric proportions, *i.e.*, by definite amounts. If we assume that besides the hydrate existing in the form of normal liquid crystals only one other richer in water can exist, its composition being given by the greatest amount of water which the liquid crystals can take up, we can explain the steady transition by supposing that the two liquid-crystalline hydrates can form mixtures in all proportions, and that these mixed crystals appear more liquid and show less deviation of the rays resulting from double refraction for equal thickness, the more they contain of the hydrate which is richer in water.

If continually increasing quantities of water, or better still (for reasons already stated) aqueous ammonia, are added to a solution of the normal liquid-crystalline mass in alcohol, the corners become more and more rounded off while the individual crystals get shorter. If the crystals were originally scarcely visible in ordinary light because their indices of refraction were nearly the same as that of the mother-liquor, as the quantity of water in the solution increases their outlines become more distinct, so that it is not necessary to use crossed Nicols in order to see them. Their extinction between the latter finally becomes abnormal, fan structures being formed at various places, probably because the leaflet-shaped molecules endeavour to arrange themselves parallel to the curved surface. If the chrysalis form changes into the spherical form the structure becomes perfectly sphaerolithic; the spheres in every position between crossed Nicols show the black cross of sphaero-crystals (Note 10).

This molecular structure, *i.e.*, the arrangement of the molecular leaflets parallel to the surface, the optical axis being everywhere perpendicular to the latter, is characteristic of the myelin forms, which are to a certain extent liquid sphaero-crystals drawn out to form little rods. Occasionally, but by no means invariably, they are hollow, *i.e.*, the liquid crystalline mass appears as a crust on a central part formed of isotropic liquid mother-liquor. The orientation of the molecules is then the result of the influence of the outer as well as the inner surface. In most cases the hollowness is only an illusion produced because the water contained in the mass alters by leaps and bounds from the interior outwards, or because the structures are on glass and at the places in question, like other liquid crystals, become semi-isotropic, and thus appear dark between crossed Nicols. The structure of myelin forms can be seen best if the alcoholic solution of the ammonium oleate, in which isolated liquid crystals have separated, is placed under a cover-glass shaped like a watch glass (concave side upwards), and ammonia is allowed to flow round it. In consequence of the contact movement the alcoholic solution makes arch-shaped incursions into the ammonia, and vigorous mixing of the two liquids takes place owing to diffusion. Just at the boundary the alcoholic solution which has diffused into the ammonia may persist. But as it presses forward and mixes more with water the ammonium oleate is precipitated in the form of very small chrysalis-like liquid crystals. There are only a few of them, as the solution mixes with ammonia only with difficulty. Conversely the ammonia penetrates into the arching parts of the alcoholic solution, and causes the formation of a precipitate of liquid crystals which unite to form a semi-isotropic crust, all the molecular axes arranging themselves perpendicularly to the surface. Thus the beginning of a kind of hollow myelin formation results, the interior being filled with alcoholic mother liquor. As the diffused water penetrates further, which is furthered by the formation of currents in consequence of contact movements, the myelin forms separate as drops which are surrounded with a liquid-crystalline skin. Numbers of such drops run together to form a frothy mass, the frothy walls of which are semi-isotropic liquid crystalline lamellæ, while the inside of the cells consists essentially of aqueous soap solution.

If instead of the alcoholic solution pure liquid crystalline ammonium oleate hydrate is used the same diffusion processes take place, but they are confined to the immediate neighbourhood of the limiting surface, and are only manifested by the effect that hydrate richer in water is formed there and continually goes over into that already present. At places where by the adsorption power of the glass this hydrate possesses semi-isotropic structure, so that the principal axes (optical axes) of the molecules are perpendicular to the surface of the glass, the same also holds good for the hydrate richer in water. The so-called oily streaks clearly appearing between crossed Nicols go continuously over into the likewise bright looking margins of the myelin forms (see "Die neue Welt der flüssigen Kristalle," 1911, p. 196; this can be seen very well on the addition of eosin, when the formation of myelin forms is very incomplete). Owing to the formation of this hydrate the consistency of the mass as well as its surface tension becomes very small at the places in question, and as the volume is increased owing to the absorption of water the projections known as "myelin forms" result. The fact that they take the form of a cylinder, and the diameter of the cylinder remains the same when further swelling up occurs, is explained by the difference of the surface tensions of the swollen and unswollen parts which always remain the same. My earlier statements (*Wied. Ann.*, 1895, lvi., 780) must thus be corrected, difference of surface tension between soap and oleic acid being replaced by that between swollen and unswollen parts. The pressing out of the snake-like apparently living crystals of para-azoxycinnamic acid ethyl ester (*Ann. Phys.*, 1906, xix., 24, Figs. 26—29) may be explained by supposing that monobromonaphthalin is more readily taken up at the flattened parts of the spheres. It may also be explained by the shaping force of the liquid crystals, the molecules of which endeavour to assume a sphaerolithic arrangement, but owing to the continued swelling up of the mass a cylinder with equal diameter and the same radical structure attaches itself to the hemisphere originally formed. The leaflet-shaped molecules are grouped in concentric circles about the axis just as in the sphaerolithic arrangement they are grouped in concentric spherical surfaces about the mid-point.

When the myelin forms come in contact with the glass both above and below them the molecular axes arrange themselves perpendicularly to the latter. Where the mass touches the glass it becomes semi-isotropic and thus appears dark between crossed Nicols; the walls only in section exhibit fan structure, as I have stated before (*Wied. Ann.*, 1895, lvi., 786, Fig. 19). It is therefore easy to be deluded into thinking that one is dealing with bubbles filled with isotropic liquid. With larger specimens, such as are formed when alcohol is added to the ammonium oleate, or if ammonium linoleate, which forms analogous liquid crystals as well as myelin forms is added, one can recognise in this apparently isotropic liquid "oily streaks" and "conical alterations of structure," which clearly show the nature of the interior of the myelin forms. After taking away the cover-glass by teasing with a mounted needle it may be proved that the interior has actually a gelatinous (or sticky) consistency. The expression is not quite correct, for a jelly is a heterogeneous substance of a

spongy or frothy nature, which in consequence of the presence of solid threads or lamellæ, or on account of the surface tension of the cell walls of the froth, shows a kind of perfect elasticity. The similar phenomenon appearing in the case of the myelin forms, that the mass after teasing endeavours to reassume its original form, and therefore appears gelatinous, on the other hand depends upon another cause, namely, the shaping force of the liquid crystals which conditions the shape of the myelin forms and differs both from elasticity and from surface tension, although, as has been said above, it is to be regarded as the effect of molecular forces.

As at least two different hydrates of ammonium oleate are concerned in the mixing it would be expected, as in other cases of the formation of mixed crystals of non-isomorphous substances (*Zeit. Kristallog.*, 1877, i., 483, 528; 1883, viii., 433; *Zeit. Phys. Chem.*, 1887, i., 15; 1891, viii., 543; *Wied. Ann.*, 1894, li., 47; "Flüssige Kristalle," 1904, pp. 150—182; "Die scheinb. lebl., Krist., 1907, p. 52; "Die neue Welt der flüssigen Kristalle," 1911, p. 122; *Verh. d. Karlsr. Nat. Ver.*, 1913, xxv.), that the structure of the myelin forms would show deviations from the normal structure just as the structure of crystal drops suffers spiral distortion owing to the presence of foreign substances, the distortion manifesting itself in the efforts of the drops to rotate, in rotation of the plane of polarisation, &c. (*Ann. Phys.*, 1900, ii., 649. 687; 1905, xviii., 808; "Flüssige Kristalle," 1904, pp. 28—34, Tables XIV. —XVII.; *Phys. Zeit.*, 1911, xii., 540; *Ann. Phys.*, 1911, xxxv., 193; *Heidelb. Sitzungsber.*, 1911, No. 22, Tables VI.—VIII.; 1912, No. 13, Table III., Fig. 64; *Ann. Phys.*, 1912, xxxix., 105). As a matter of fact the myelin forms show a tendency to rotate, the result of which is that if a cylindrical thread cannot turn freely, for instance, because the end is twisted and touches the glass, or because it has run into the swelling mass, the one part of the thread twists round the other or they both form a double spiral.

The supposition that the myelin forms are of the nature of mixed crystals is confirmed by their frequently stratified structure, which can be explained only by a difference in the character of the deposited layers. As these layers have everywhere the same thickness, although the myelin form steadily grows, it follows that the later layers are not simply denosited on the former, as in ordinary stratified mixed crystals, but that the structure grows by interpenetration of water molecules (swelling up), just as the growth of an organism is due not to apposition but to intussusception. Even foreign substances can be taken up in the myelin forms, but they possess the same power of sell purification as other crystals (*Zeit. Kristallogr.*, 1877, i, 487; "Molekular-physik," 1888, i., 345; "Flüssige Kristalle," 1904, p. 137; "Die neue Welt der flüssigen Kristalle," 1911, p. 330; *Phys. Zeit.*, 1910, xi., 44; *Umschau*, 1910, xiv., 950). Thus, for example, if different aniline colours are added to the ammonium oleate or ammonia, the myelin forms do not take up the colour. Prepared myelin forms only become a faint blue very slowly in an ammoniacal solution of methylene blue, even if the concentration of the dye is very high. But if they are formed in such a solution they acquire an intense pure blue colour, while the solution is decolorised. (The colour of the solution is more violet than blue). Probably a new compound is formed which can only slightly diffuse into the liquid crystals, or not at all, but which can be deposited to a considerable extent if it is firmly bound by the adsorption power during the growth of the crystal. The effect is even more striking if in the preparation of myelin forms instead of pure ammonia the almost colouriess solution of gentian violet in ammonia is used. The freshly formed myelin forms become deep violet, although both solutions, in the mixed zone of which they appear, are colourless. As the formation of the myelin forms is only a little influenced by the addition of dyes, their use is to be recommended for demonstrations of the phenomena, for the intensely coloured structures stand up well against the colourless ground (Note 11).

To a certain extent the myelin forms can absorb ammonium ricinoleate, which gives the same liquid crystals as oleic and linoleic acids. The formation of myelin forms ceases, however, when the percentage is large, as would be expected, for ammonium ricinoleate cannot yield myelin forms of itself, probably because it is too readily soluble in aqueous ammonia.

On projection the myelin forms always appear yellowish on a white ground. There seems to be a sort of dissipation of light as in the Tyndall effect, which must be caused by the deviation of the molecules from parallelism.

When the action of the water (or better still, ammonia) is continued, the arrangement of the molecules in myelin forms is finally lost, and they disappear, giving, as has been already said, a soap solution. By the addition of salts (ammonium chloride or bromide) and some alcohol, chrysalis-like structures can be precipitated from such solutions; these must be regarded as hollow liquid crystals, the interior of which is filled with isotropic liquid. First of all droplets of concentrated oleate solution separate out, and on their surfaces, in consequence of continued electrolytic action, a semi-isotropic liquid-crystalline skin is formed. By the flowing together of such hollow sphaerocrystals complicated structures result, which like masses of froth are divided internally into several divisions by plane (liquid crystalline) lamellæ (Note 12).

The swelling up of liquid crystals recalls the swelling up of starch grains, which show a black cross between mixed crystals, and are thus probably sphaerolithic formations (*cf.*, on the other hand, G. Malfitano and A. Moschikoff, *Comptes Rendus*, 1913, clvi., 1412) or crystals of white of egg (Schimper, *Zeit. Kristallog.*, 1881, v., 131; St. Bondzynski and L. Zoja, *Zeit. Phys. Chem.*, 1894, xix., 1; A. Wichmann, *Ibid.*, 1899, xxvii., 575), which can take on an intense coloration, or hæmoglobin crystals (A. Rollet, *Sitzungsber. der Wiener Akad.*, 1862, [2], xlvi., 65). The absorption of foreign substances by zeoliths and other solid crystals (F. Rinne, "Fortschritte der Mineralogie, Kristallographie, und Petrographie," 1913, iii., 159) may be an allied phenomenon, as also the migration of silver ions in silver iodide crystals (O. Lehmann, *Wied. Ann.*, 1889, xxxviii., 396) and the artificial coloration of crystals by radium rays (C. Doelter, "Das Radium und die Farben," Dresden, 1910), phenomena which show that the structure of crystals can be obtained by the molecular directive force, in spite of the loosening influence of thermic motion. Since new molecules are obtained by the puffing up, the preservation of the structure must be due to the fact that the new molecules are regularly arranged in consequence of the molecular directive force, as in polymorphic changes (*Zeit. Kristallogr.*, 1877, i., 107), and the solution of hydrated salts (*loc. cit.*, p. 102, Table V., Figs. 1—4). We are forced to the conclusion that the diffusion of water dees not take place under the influence of osmotic pressure as the theory of "solid solutions" assumes, *i.e.*, by the interpenetration of molecules of water between the molecules of crystals, but (as in the migration of ions) from molecule to molecule, in such a way that molecules at the surface which have taken up water give it up to inner molecules containing less water, and that it is then similarly passed on to molecules which are still further in and are poorer in water. Swelling up thus consists in continual dissociation and reproduction of molecules containing water, according to the law of mass action.

Notes.

8. The displacement of the rays seems to be the same for equal amounts of the original substance.

9. The experiment which I brought forward in favour of the influence of oleic acid was faulty (*Wied. Ann.*, 1894 lvi., 776, Fig. 2). Apparently an accidental current in the liquid produced the opposite effect to that which ought to have been seen. The myelin forms hardly appear, or are altogether absent where there is free oleic acid, but are very abundant where no oleic acid is present. To a

very small extent they result from acid ammonium oleate, and then only because some neutral oleate is formed by contact with water.

10. Specially fine crystals of this kind can be obtained by cooling hot solutions of cholesterin with cetyl alcohol or elaidinic acid in a very little alcohol. As they separate they fall into a state of rapid motion, which is due to the local change of composition of the solution caused by the separation; this change of composition leads to differences of surface tension, and hence contact movement like that of camphor on water. It recalls the Brownian molecular movement. During the formation of myelin forms in water, when growth and solution continually alternate, sometimes violent movements which have the same origin occur.

11. G. Quincke (*loc. cit.*) has also observed the absorption of methylene blue, but he ascribes it to the hypothetical envelope of oleic acid, as oleic acid takes up the colour from aqueous solutions.

12. In some cases I also obtained comma shaped structures, club-shaped at one end, and diminishing by degrees towards the other. I could not determine the conditions with great accuracy, but they seemed to be myelin forms, the structure of which is greatly altered by the presence of foreign substances. They appeared in a commercial gelatinous ammonium oleate which with ammonia alone gave no myelin forms, but only on addition of salt.

THE ATOMIC WEIGHT OF TELLURIUM, AND A CRITIQUE OF THE BASIC NITRATE METHOD OF DETERMINATION.

By WM. L. DUDLEY and PAUL C. BOWERS.

THIS work is a continuation of the investigation of tellurium, begun by Dudley and Jones, who made a spectrographic study of it (*Journ. Am. Chem. Soc.*, xxxiv., 995). Our object, in the beginning, was to make atomic weight determinations of different fractions of tellurium precipitated by hydrazine hydrochloride, and thus to confirm the conclusions reached by Dudley and Jones, that tellurium did not suffer decomposition when so treated; but later it was found desirable to make an investigation of the basic nitrate method for determining the atomic weight.

The tellurium used in this investigation was purified as described by Dudley and Jones (*loc. cit.*) There were in all twenty fractions of the tellurium, about 6 grms. to the fraction, precipitated by hydrazine hydrochloride. The spectrograms taken of the different fractions showed no impurities, with the exception of the last one.

Unless otherwise stated Kahlbaum's chemically pure reagents were used. Ammonia-free water was used for all dilutions.

Very concordant results have been obtained by Köthner (*Ann.*, cccxix., 1), Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675), and Flint (*Am. Journ. Sci.*, [4], xxx., 209) with the basic nitrate method. Therefore we began the work by using this method. Our procedure was as follows:—The tellurium was dissolved in nitric acid (sp. gr. 1·25), and evaporated on a steam-bath at about 70°. The basic nitrate which crystallised out was washed with concentrated nitric acid, and then dried by heating at 120° in a current of air dried by sulphuric acid and phosphorus pentoxide. These crystals were then ground in an agate mortar. Portions were weighed in a platinum crucible, and brought to constant weight by heating in a current of dry air at a temperature of 140° for periods of twenty-four hours each. The crucible was then placed over a low Bunsen flame, and the temperature very slowly and gradually raised to the fusion-point of the dioxide.

A Freas electric oven was used for drying the crystals and bringing the basic nitrate to constant weight. This oven was regulated to vary only a fraction of a degree. In order to draw the air over the basic nitrate, a specially constructed glass apparatus was made to fit into the oven.

The fractions Nos. 1 and 2, when dissolved in nitric acid, gave to all appearances the orthorhombic crystals of the basic nitrate, but from the solution of the third fraction, there separated colourless crystals of perfect octahedral form. These proved to be crystals of tellurium dioxide. They dissolved with difficulty in a large excess of nitric acid (sp. gr. 1·25). But from this nitric acid solution of the dioxide there would usually separate, on concentration, the orthorhombic crystals of the basic nitrate, but sometimes it would separate as the dioxide again.

Thinking that there might be some difference between the tellurium which came down in the octahedral form as the dioxide and that crystallising in the orthorhombic form as the basic nitrate, samples of the two were reduced to the elementary state (tellurium), and spectrograms were taken of each. A comparison of the spectra was made but no difference was noted. In order to be sure of this point, it was decided to make atomic weight determinations of them, so whenever the dioxide crystals appeared they were separated from the liquid by decantation, washed with concentrated nitric acid, dissolved in nitric acid, sp. gr. 1·25, and the solution evaporated until the orthorhombic crystals separated. Sometimes the dioxide crystals would again appear on concentration, as previously mentioned. These were treated with more nitric acid (sp. gr. 1·25), and the operation repeated until only the crystals of the basic nitrate form were obtained. In fraction No. 15 especial effort was made to avoid the formation of any dioxide crystals, by dissolving in a very large excess of acid. Then only the orthorhombic crystals were obtained from the solution, but they were found to contain inclusions of the dioxide.

As the amount of basic nitrate obtained from the different fractions was not enough for a series of atomic weight determinations, the crystals of the fractions Nos. 1, 2, 3, and 4, and Nos. 5, 6, 7, and 8, &c., first separating in the orthorhombic form were put together, and the crystals of the dioxide which were converted into the basic nitrate were grouped in like manner.

Portion.	Fraction Nos.	Det. No.	$2TeO_2HNO_3$. Grms.	TeO_2. Grms.	TeO_2. Per cent.	Atomic wt.
A	1, 2, 3, and 4	1	1·74464	1·46204	83·796	130·94
A	1, 2, 3, and 4	2	1·08072	0·90445	83·689	129·65
A	1, 2, 3, and 4	3	1·93538	1·61476	83·434	126·69
A	1, 2, 3, and 4	4	1·34715	1·60841	83·750	130·39
A	1, 2, 3, and 4	5	1·33704	1·59490	83·832	131·37
A	5, 6, 7, and 8	6	2·27174	1·91397	84·251	136·56
A	5, 6, 7, and 8	7	1·61049	1·35653	84·230	136·61
A	5, 6, 7, and 8	8	1·67029	1·40286	83·976	133·13
B	1, 2, 3, and 4	9	1·55380	1·38070	83·391	126·13
B	1, 2, 3, and 4	10	1·26647	1·05595	83·377	126·04
B	5, 6, 7, and 8	11	1·74197	1·45398	83·455	126·93
B	5, 6, 7, and 8	12	1·19549	0·99758	83·428	126·62
B	11 and 12	13	0·59279	0·49295	83·157	123·58
B	11 and 12	14	0·60778	0·50670	83·396	125·95
B	15	15	1·62585	1·39745	85·952	160·78
B	15	16	1·28903	1·09327	84·813	143·96

The preceding are the results obtained. For convenience of tabulation, the determinations of the portions first crystallising as the dioxide are marked "A" and those separating from the original solution in the orthorhombic crystals of the basic nitrate, "B."

In all of the atomic weight determinations the weighing was made by the method of oscillations. The set of weights used was standardised, and the weighings were reduced to vacuum.

As the results were so irregular the method was necessarily abandoned. According to our experience there is no certainty of the purity of the basic nitrate crystals. From a nitric acid solution the tellurium may crystallise

as tellurous acid, tellurium dioxide, and the basic nitrate of tellurium according to the temperature and excess of acid present. Thus the conditions for crystallisation must be very exact in order to obtain pure crystals of either. What all of these conditions are we are not prepared to say. The temperature may be regulated and before evaporation a large excess of acid may be present; but on concentrating the solution it often becomes supersaturated, and there is not sufficient nitric acid present to form the basic nitrate with all of the tellurium. So the dioxide either crystallises out or is held as an inclusion in the orthorhombic crystals of the basic nitrate. Such inclusions were observed on close examination with the microscope. Also when the dioxide and basic nitrate are together, some of the dioxide is always held between the basic nitrate crystals, which have a tendency to form rosette clusters. This tends toward high results, and with one exception determinations marked "A" gave high results. The crystals from the solution of fraction "B," No. 15, also contained these inclusions. Although, as said above, only orthorhombic crystals separated from this solution, still they gave the highest results, owing to the amount of dioxide included.

In all of the determinations marked "B" in which the basic nitrate was crystallised out after the dioxide crystals had been separated from the solution, low results were obtained. These low results were due to inclusions of the mother-liquor, instead of the dioxide, as in the case of high results. These inclusions were also observed under the microscope. Baker and Harcourt (*Journ. Chem. Soc.*, xcix., 1311) conclude from their investigations that some of the trioxide basic nitrate may be formed in small amounts along with the dioxide basic nitrate of tellurium, and in this way they attempt to account for the low results of Flint.

That some of the dioxide may be lost mechanically by the gases evolved when the nitrate is decomposed by heating should also be taken into consideration. But only in one or two instances was there any evidence of this on the lid of the crucible, and these determinations were discarded. Then there is the uncertainty as to whether all the oxides of nitrogen are driven off at the fusion-point of the dioxide. For all of the reasons given above we have come to the conclusion that this method is not dependable.

The Tetrabromide Method.

Owing to the failure of the basic nitrate method to give reliable results, we adopted the tetrabromide method for determining the atomic weight of the fractionally precipitated tellurium. The tetrabromide method presented by Baker and Bennett (*Journ. Chem. Soc.*, xci., 1849) is very simple, and avoids the danger of loss due to transferring of material from one vessel to another, and the authors got exceedingly concordant results.

Baker's "Analysed Bromine" containing from 0·26 to 0·46 per cent of chlorine was purified according to the method given by Stas. A pound of bromine was distilled over chemically pure zinc oxide and potassium bromide, ten times the amount of each required for the chlorine present being used. The bromine was then treated with phosphorus pentoxide in a separatory funnel, and allowed to stand for several hours. Finally, the bromine was drawn off and re distilled.

Each fraction of the tellurium which had been converted into the basic nitrate for the previous method was twice evaporated to dryness with hydrochloric acid, then dissolved in hydrochloric acid, diluted to the precipitating point of the tellurium dioxide with ammonia-free water, and sulphur dioxide passed into the hot solution. The tellurium thus precipitated was filtered through hardened filter-paper, washed first with hydrochloric acid, 1 : 1, then warm hydrochloric acid, 1 : 4, ammonia free water until free of the chloride, and finally alcohol followed by ether. This was dried in a vacuum over sulphuric acid in order to avoid oxidation of the finely-divided particles of tellurium. More sulphur dioxide was passed into the filtrate, and the process repeated until all of the tellurium was precipitated. The dried precipitated tellurium was then fused into sticks, after the method used by Dudley and Jones (*loc. cit.*), for the preparation of electrodes.

Portions of this fused tellurium were powdered in an agate mortar, and placed in the lower bulb of the weighed tube, which was specially constructed of Jena glass according to the diagram given by Baker and Bennett (*Journ. Chem. Soc.*, xci., 1857). This was dried to constant weight by heating in the electric oven at 50° in a current of air dried by calcium chloride, sulphuric acid, and phosphorus pentoxide. The air was then displaced by nitrogen. The nitrogen was obtained by passing air over red-hot copper turnings, then through a potassium hydroxide solution of pyrogallic acid, and was dried in the same way as the air. The purified bromine was run into the upper bulb of the tube through a funnel with a drawn-out stem, and then the tube was tightly capped. The bromine was run down into the tellurium a little at a time, until the tellurium was all converted into the tetrabromide, and some excess of liquid bromine remained. This was allowed to stand for about twenty-four hours. The tube was then placed in the electric oven, and heated to 50°, while a current of dry nitrogen was drawn through it. When no tests for bromine with potassium-iodide starch paper was obtained in the nitrogen drawn through the tube, the oven was allowed to cool to room temperature. The nitrogen was then displaced by dry air and the tube weighed. A similar tube was used as a counterpoise.

Concordant results were not obtained from the tellurium precipitated and cast in sticks as described. Notwithstanding washing with hydrochloric acid, drying in a vacuum, and fusion in hydrogen, the tellurium contained some dioxide, and, as was discovered later, some impurities. Parts of the series 1, 2, 3, and 4; 5, 6, 7, and 8; 11 and 12, A and B were put together, and distilled in hydrogen. A residue of about 0 1 per cent was left in the boat. This residue was found to contain some carbon, which was very probably due to the hydrogen, although it was generated from chemically pure zinc and hydrochloric acid; a slight trace of iron which must have come from the can of liquid sulphur dioxide, as no iron lines were previously found in the spectra of the tellurium; some tellurium and microscopic fragments of glass, due to shattering the glass tube to remove the fused tellurium. This tellurium, when re-distilled, left only a slight coloration in the boat, showing that the one re-distillation was sufficient to purify the material. The results of the determinations are as follows:—Br = 79·92.

	Wt. of Te. Grm.	Wt. of $TeBr_4$. Grms.	Te in $TeBr_4$. Per cent.	At. wt. of Te
No. 1	0·479816	1·682387	28 520	127·550
No. 2	0·296341	1·037049	28·575	127·897
No. 3	0·433241	1·516746	28·563	127 819
No. 4	0·457782	1·605684	28·510	127·487
No. 5	0·321522	1·126939	28·530	127·612

The high results in these determinations were due to some tellurium which was left in the bulb unattacked by the bromine. This was caused by running the bromine into the lower bulb too rapidly; thus inclusions of tellurium were formed in the tellurium tetrabromide which could not be broken up by shaking the tube. It is best to start with smaller quantities of tellurium than those used above, because it allows better mixing of the material, and thus brings the bromine into contact with all of the tellurium.

The remainder of the portions "A," Fractions Nos. 1, 2, 3, and 4, "B." Fractions, 1, 2, 3, and 4, also the Fraction No. 19 of the tellurium precipitated by hydrazine hydrochloride were distilled separately in hydrogen, and the atomic weight determinations gave the following:—

Fraction Nos.	Det. No.	Wt of Te. Grm.	Wt. of $TeBr_4$. Grms.	Per cent of Te.	At. wt. of Te.
A 1, 2, 3, and 4	1	0·300558	1·054251	28·509	127·481
A 1, 2, 3, and 4	2	0·199807	0·700947	28·505	127·456
B 1, 2, 3, and 4	1	0·22032	0·773048	28·500	127·425
B 1, 2, 3, and 4	2	0·158161	0·554717	28·512	127·500
19	1	0·436907	1·532360	28·512	127·500
19	2	0·29811	1·045485	28·514	127·512
		Average		28·509	127·479

These determinations show that there is no separation of the tellurium after 19 fractional precipitations by hydrazine hydrochloride, and that there is no difference between the tellurium which crystallised from the nitric acid solution in the octahedral crystals as the dioxide and that separating in the orthorhombic crystals as the basic nitrate.—*Journal of the American Chemical Society*, xxxv., No. 7.

A STUDY OF THE METALLIC TELLURITES.*

By VICTOR LENHER and EDWARD WOLESENSKY.

(Concluded from p. 206).

Magnesium Tellurite. — This substance was obtained from a solution of magnesium chloride by adding a solution of sodium tellurite. It is a white flocculent precipitate, which is slightly soluble in water. On standing for a time in the mother-liquor or in water, it becomes granular and heavy. The composition of the precipitate is not affected by varying the proportion of the two salts from which it is formed.

This tellurite was found to have the composition $5MgTeO_3.9H_2O$.

Calculated.—Mg, 10·84; Te, 54·91; H_2O, 13·94.
Found I.—Mg, 9·98; Te, 55·29; H_2O, 13·48.
Found II.—Mg, —; Te, 54·91; H_2O, 13·62.
Found III.—Mg, 9·91; Te, 55·39; H_2O, 13·65.
Found IV.—Mg, 9·70; Te, 55·10; H_2O, 14·29.
Found V.—Mg, 9·93; Te, 55·59; H_2O, 13·36.

In the above table, numbers I., II., and III. were precipitated from solutions containing excess of sodium tellurite, while IV. and V. were precipitated from solutions containing an excess of magnesium chloride.

Owing to the somewhat unusual ratio of the water to magnesium tellurite in this compound, a more careful study was made of this relation. A quantity of the dried precipitate, equivalent to 1 grm. of anhydrous tellurite, was heated at various temperatures until the weight became constant. Then, from the total water content and the loss in weight at each temperature, it was possible to calculate the amount of water still retained.

Temp.	H_2O held by 1 g. $MgTeO_3$.	Temp.	H_2O held by 1 g. $MgTeO_3$.
20°	0·1545	260°	0·0758
100°	0·1360	300°	0·0250
130°	0·1170	330°	0·0130
175°	0·0965	360°	0·0080
200°	0·0860	400°	0·0050
220°	0·0838	450°	None

If these results are plotted in a curve it will be seen that at about 260° there is a sharp break in the curve, and that the amount of water retained at this temperature is very nearly one-half of the original amount, 0·1545 grm. Above this temperature there is a rapid falling off in the water content, until at 450° all the water can be driven off in fifteen minutes.

This experiment indicates that between 450° and ordinary temperature, there exist at least two definite hydrates of magnesium tellurite, namely, $5MgTeO_3.9H_2O$, and $10MgTeO_3.9H_2O$. It might also be noted that the composition at 100°, as calculated from the above results, is $2MgTeO_3.3H_2O$ although this may have no special significance, since no data were obtained for temperatures below 100°. It is also quite evident that most of the water in this compound is quite firmly held.

Barium Tellurite.—To obtain this substance, a solution of sodium tellurite was added to a solution of barium chloride. A white flocculent precipitate was obtained, which was only slightly soluble in water. Attempts were made to obtain barium tellurite in crystalline form but were unsuccessful. Analysis of different samples showed a considerable variation in composition. Investigation showed that the precipitates always contained barium chloride, and sometimes in considerable quantities. This barium chloride could not be washed out completely by repeated and long-continued boiling with large quantities of water. Accordingly the precipitation was performed in dilute solutions, containing exactly equivalent quantities of the two salts. Even under these conditions the precipitates always contained small amounts of barium chloride which could not be washed out.

The analysis of this substance was carried out in the following way. Water was determined as usual. The chlorine was determined by precipitation with silver nitrate, from a nitric acid solution of the barium tellurite.

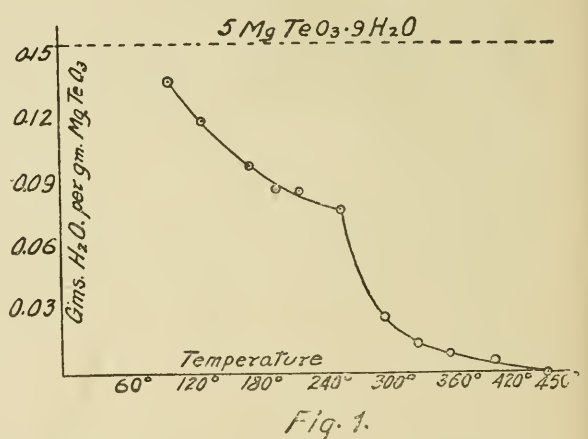


Fig. 1.

After removing the excess of silver nitrate by adding hydrochloric acid, the barium was precipitated by means of ammonium sulphate. The filtrate from the barium sulphate was evaporated to dryness, and the residue treated repeatedly with hydrochloric acid to remove all of the nitric acid. Finally from this hydrochloric acid solution the tellurium was precipitated by sulphur dioxide and hydrazine hydrochloride. The method of volatilisation in hydrochloric acid gas could not be used in this case, since all of the tellurium could not be driven off without raising the temperature so high that barium chloride would volatilise.

The proportion of barium to tellurium was greater than the normal salt should have. But in all cases the precipitates also contained chlorine in appreciable quantities. If the chlorine contained be calculated as barium chloride, and the tellurium as normal barium tellurite, the results agree with the analysis obtained. This is particularly evident in those samples which were precipitated in presence of excess of barium chloride.

Several samples were analysed, in all of which the proportions of barium chloride, tellurite, and water varied considerably. The following analyses are typical examples. The first sample was precipitated in presence of excess of barium chloride; the second one from equivalent quantities of this salt and sodium tellurite.

* *Journal of the American Chemical Society*, xxxv., No. 6.

1. Calculated for $8BaTeO_3 5BaCl_2 4H_2O$.—Ba, 49·50; Te, 28·29; Cl, 9·82; H_2O, 1·99.
   Found.—Ba, 48·68; Te, 29·23; Cl, 9·43; H_2O, 1·90.
2. Calculated for $20BaTeO_3 \frac{1}{2}BaCl_2 20H_2O$.—Ba, 41·89. Te, 37·95; Cl, 0·53; H_2O, 5·35.
   Found.—Ba, 41·83; Te, 38·33; Cl, 0·53; H_2O, 5·07.

Cadmium Tellurite.—This salt was obtained as a white amorphous insoluble precipitate, by the interaction of cadmium chloride and sodium tellurite.

In its analysis the method of volatilisation could not be used for the separation of the tellurium, on account of the volatillty of cadmium chloride. The tellurium was therefore first precipitated from a hydrochloric acid solution of the material by means of sulphur dioxide and hydrazine hydrochloride. In the filtrate from the tellurium, the cadmium was determined in one of two ways. (1) The solution was evaporated to dryness, the residue taken up in water, and the cadmium precipitated as carbonate by means of potassium carbonate, and weighed as oxide. (2) The solution was first neutralised with potassium hydroxide, and potassium cyanide was added until the precipitate first formed just dissolved. This solution was then electrolysed, using a current density of 0·5 to 0·8 amperes per 100 sq. cm., with about 4 to 4·5 volts. After five hours the voltage was increased to 5 volts for an hour.

The composition found did not agree with the normal tellurite. The tellurium was always slightly high and the cadmium correspondingly low. The following gives the average composition found, together with the calculated results for $3CdTeO_3.2H_2O$.

Calculated.—Cd, 37·47; Te, 42·53; H_2O, 4·00.
Found.—Cd, 36·09; Te, 44·20; H_2O, 3·67.

The regular discrepancies appearing in the analysis are explained by the fact that when tellurium is precipitated in the presence of cadmium, it carries down some of the cadmium with it. This is made quite evident from the following experiments.

I. Some tellurium which had been precipitated in the presence of cadmium was dissolved in aqua regia and the solution evaporated to dryness. The residue was then taken up in dilute hydrochloric acid and precipitated by means of hydrogen sulphide. This precipitate was digested for several hours in a warm place with yellow ammonium sulphide. The residue left by the ammonium sulphide was treated with hot concentrated hydrochloric acid and filtered. After nearly neutralising the filtrate with potassium hydroxide, it was treated with hydrogen sulphide. A small amount of cadmium sulphide was obtained.

II. A weighed amount of pure tellurium dioxide was mixed with cadmium chloride (about 0·8 grm.). After dissolving in hydrochloric acid, the tellurium was precipitated with sulphur dioxide and hydrazine hydrochloride. The following results were obtained:—

Te found.—0·7037. Calculated.—0 6929.
„ 0·9476. „ 0·8754.

It will be noted that the apparent weight of the tellurium precipitated was in each case considerably greater than the calculated amount.

III. A determination of tellurium by means of sulphur dioxide and hydrazine hydrochloride was made in a weighed amount of pure tellurium dioxide. The tellurium thus obtained was again dissolved and the determination repeated. The results were as follows:—

Te found.—0·4045. Te used.—0·4052.
„ 0·4034. „ 0·4045.

IV. Exactly equivalent quantities of cadmium chloride and sodium tellurite, both in solution, were brought together, and the resulting precipitate filtered off. The clear filtrate was evaporated o a small bulk and treated with hydrogen sulphide. No precipitate was formed, showing that both cadmium and tellurium had been completely removed in the first precipitate. This precipitate, therefore, could have been nothing other than the normal tellurite.

Silver Tellurite.—When a solution of sodium tellurite is added to a solution of silver nitrate, a pale lemon-yellow flocculent precipitate is formed. This precipitate remains pale yellow as long as the silver nitrate is in excess, but when sodium tellurite is added in excess the colour of the precipitate quickly changes to white. On drying, both precipitates assume a buff colour, and are almost indistinguishable from each other. On standing, however, the one which was precipitated in presence of an excess of silver nitrate begins to turn dark in colour, and in the course of a week or two has changed completely to a dark bluish grey colour. The other does not change, and has actually been kept for twenty months without undergoing any modification.

Nevertheless, both of these precipitates have the same composition, and when dried both are anhydrous. In the following Table I. and II. were precipitated in presence of an excess of silver nitrate, while in III. and IV. the proportion was reversed.

Calculated for Ag_2TeO_3.—Ag, 55·14; Te, 32·59.
Found I.—Ag, 55·09; Te, 32·96.
Found II.—Ag, 54·90; Te, 32·51.
Found III.—Ag, 54·89; Te, 32·52.
Found IV.—Ag, 55·25; Te, 32·52.

Silver tellurite can exist in still other forms. When heated to a temperature of 250°, it becomes deep blue or purple in colour. This change takes place without any change in weight. On heating still higher, to 450° or 5·0°, it again changes to a pale yellow. In this last condition it can be cooled down to ordinary temperatures unchanged, providing it is not disturbed during the cooling. But if during this cooling, and while it is still quite hot, it is disturbed by compression with a glass rod, the mass immediately changes to the purple variety.

Again, when freshly precipitated silver tellurite is treated with ammonium hydroxide it dissolves immediately, and when the solution is allowed to evaporate spontaneously brownish yellow crystals deposit. These crystals contain neither ammonia nor water, and can be heated to 500° or higher without any change in weight. On cooling, after being thus heated, these crystals again yield the ordinary pale yellow silver tellurite.

It thus appears that silver tellurite can exist in a number of different varieties. The freshly precipitated salt is soluble in acetic and tartaric acids, also in nitric and sulphuric acids. Hydrochloric acid decomposes it with the formation of silver chloride and tellurium tetrachloride. It is insoluble in water.

An attempt was made to obtain silver tellurite in crystalline form in the same way in which Hutchins crystallised some of the precipitated tellurates (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1157). The method was to allow the precipitate to stand in contact with water containing minute quantities of free acids. This method, however, proved unsuccessful with the tellurites. It might be stated that the precipitated tellurites as a rule show very little or no tendency to pass into the crystalline state.

Nickel Tellurite.—$NiTeO_3.2H_2O$ was obtained as a pale greenish yellow precipitate on adding a solution of sodium tellurite to a solution of nickel chloride. The precipitate was light and amorphous.

Calculated.—Ni, 21·72; Te, 47·21; H_2O, 13·32.
Found.—Ni, 21·40; Te, 47·96; H_2O, 13·62.

When heated, the light yellow green tellurite loses water and turns to a light brown colour.

Cobalt Tellurite.—$CoTeO_3.H_2O$ was obtained by precipitation from a solution of cobalt chloride as a dark,

purple-blue insoluble substance. When heated to 300—400° it melts without change of colour, losing water at the same time.

Calculated.—Co, 23·36; Te, 50·52; H_2O, 7·12.
Found.—Co, 23·39; Te, 50·30; H_2O, 7·79.

Manganese tellurite is a very unstable compound. When a solution of manganous chloride is added to a solution of sodium tellurite, there forms a voluminous white precipitate, which is faintly pink or flesh-coloured. On standing, the colour gradually changes to a deep chocolate-brown. The change takes place more rapidly when it is brought into direct contact with air. This change is due to oxidation of the manganese to the trivalent state. When the chocolate coloured substance is treated with hydrochloric acid, a dark, greenish brown solution of manganic chloride is formed. This colour is discharged by diluting the solution with water, or by boiling; in the latter case chlorine is evolved.

If the precipitation is carried out with solutions which have been previously thoroughly boiled to expel the air, the precipitate is perfectly white, and remains so as long as contact with air is avoided.

The extent of oxidation was determined by boiling the material with hydrochloric acid, distilling the chlorine into a solution of potassium iodide, and titrating the iodine with sodium thiosulphate. The tellurium was precipitated from the hydrochloric acid solution by sulphur dioxide and hydrazine hydrochloride. Finally the manganese in the filtrate from the tellurium was precipitated as manganese ammonium phosphate, ignited to pyrophosphate, and weighed. The water was estimated by difference.

The atomic ratio of manganese to tellurium was found to be 1 : 1, so that the precipitate first formed was undoubtedly normal manganous tellurite. The ratio of active oxygen to manganese, however, was less than would be required for complete oxidation of the manganese to the trivalent condition, and this ratio also varied in different samples. One sample of the freshly prepared precipitate was washed by decantation, and suspended in water, while air was bubbled through the mixture for a week. Analysis showed that only about 28 per cent of the manganese was oxidised.

The freshly precipitated manganese tellurite seems to be more sensitive toward oxygen than after it has stood for some time. White manganese tellurite was prepared by bringing together under a layer of melted paraffin freshly boiled and air-free solutions of manganese chloride and sodium tellurite. The precipitate was allowed to stand unoxidised for a week, after which it was treated for two weeks with a current of air, as in the previous case. The colour changed to brown. A determination of the active oxygen indicated that about 20 per cent of the manganese had been oxidised.

Another sample of the precipitated manganese tellurite was dried, pulverised, and left in contact with air for three weeks. At the end of this time about 38 per cent of the manganese was oxidised, and the powder had the following composition :—$3Mn_2O_3.10MnO.16TeO_2.10H_2O$.

Calculated for $3Mn_2O_3.10MnO.16TeO_2.10H_2O$.—Mn, 22·46; Te, 52·11; Active O, 1·22; H_2O, 4·59.
Found. Mn, 22·26; Te, 52·39; Active O, 1·24; H_2O, 4·49.

It is probable that complete oxidation of the manganese would be accomplished in time.

Lead Tellurite.—This compound was prepared by precipitation from a solution of lead nitrate. It forms as a white flocculent precipitate.

Calculated for $3PbTeO_3.2H_2O$.—Pb, 52·45; Te, 32·35; H_2O, 3·04
Found.—Pb, 52·09; Te, 32·26; H_2O, 3·20.

Oxidation of the Tellurites.—Shortly after the work on the tellurites was undertaken it was discovered that many of the tellurites oxidise when heated in the air under certain conditions. This fact seemed to have escaped the notice of Berzelius and other investigators, as no mention of it has been found in the literature. On account of this oxidation it is not possible to prepare the tellurites, free from tellurates, by the fusion of tellurium dioxide with carbonates, as suggested by Berzelius, without first excluding air from the mixture. Hence, in the preparation of the alkaline tellurites, the fusion was carried out in an atmosphere of carbon dioxide, as already mentioned. Tellurites which are thus prepared are completely free from tellurates, but when the precaution to exclude air during the fusion is neglected, the product always is contaminated to a greater or less extent with tellurate.

In order to ascertain how far it is possible to oxidise the tellurites by heating in the air, the following experiment was carried out. Some potassium tellurite was finely pulverised, and then spread out in a thin layer on the bottom of a crucible. The crucible was partly immersed in a bath of melted lead whose temperature was kept at 460—470°. At intervals, portions of the material were removed for analysis. The proportion of tellurate was determined by boiling the mixture with hydrochloric acid, distilling the chlorine into a solution of potassium iodide, and titrating the iodine with sodium thiosulphate. The results are given in the following table, which gives the time of heating together with the corresponding amount of potassium tellurate.

Time (in hours).	K_2TeO_4 (per cent).
10	26·88
20	52·88
30	80·99
38	94·49
43	97·86
57	99·47

The final product was next analysed with the following results :—

	Found.	K_2TeO_4.
K	29·11	29·01
Te	47·02	47·28

In this connection it is interesting to note that when potassium tellurate is heated to redness, it loses oxygen and is reduced to tellurite. Thus between 450° and red heat we have a reversal of the reaction.

$$2K_2TeO_3 + O_2 \rightleftharpoons 2K_2TeO_4.$$

Normal sodium tellurite behaves in a manner exactly similar to the potassium tellurite.

Time of heating (in hours).	Na_2TeO_4 (per cent).
10	35·09
20	64·77
30	90 76
40	99·09
50	99·49

While the normal alkaline tellurites can be oxidised quite readily, the ditellurites behave somewhat differently. Potassium ditellurite can be oxidised, but the reaction proceeds much more slowly than in the case of the normal salt. Furthermore, only one-half of the tellurium seems to be oxidisable to the higher state of oxidation. The experiment was carried out in the same way as with the normal tellurites except that the temperature was kept at 440 450°, on account of the lower melting-point of the ditellurite. The results obtained were as follows :—

Time of heating (in hours).	Active O (per cent).
19	1·18
46	2·00
89	2·81
156	3·28
221	3·54

The content of active oxygen required by the formula $K_2OTeO_3.TeO_2$ is 3·72 per cent, and that for complete conversion to ditellurate would be 7·18 per cent. It will be seen that the content of active oxygen seems to approach the former figure as a limit.

The ditellurite of potassium is white, but when it is oxidised as above, it is slightly brown in colour. This brown product belongs to a class of compounds which are formed as intermediate products in the oxidation of tellurium dioxide to trioxide, by means of alkaline oxidising agents. These compounds Berzelius thought to be tetratellurates, but they have been shown by the work of Lenher and Potter (*Journ. Am. Chem. Soc.*, 1909, xxxi., 24) to have a more complex as well as variable composition. Their composition might be represented by the general formula $m(K_2O).n(TeO_3).p(TeO_2)$, in which m, n, and p may be all different or all alike. These substances have been obtained by fusing tellurium dioxide with potassium nitrate or chlorate, and also synthetically by heating the dioxide with potassium tellurate. In the oxidation of the ditellurite of potassium to $K_2OTeO_3.TeO_2$, as described above, we are approaching the same class of compound from another direction. In this case, however, the composition is simpler and more definite.

Sodium ditellurite was also heated in the same way as the corresponding potassium salt, but after five days of heating it showed only a slight trace of oxidation. Neither the tetratellurites nor pure tellurium dioxide show any oxidation under similar treatment. It is therefore evident that with a higher content of tellurium dioxide the power of the tellurites to take up oxygen from the air decreases.

The normal tellurites of most of the other metals, with the exception of silver, can also be oxidised, but the rate of oxidation is very much lower than in the case of the normal tellurites of the alkali metals.

It has been stated, in describing the methods of analysis, that water was usually determined by loss of weight on heating. In view of the fact that the tellurites take up oxygen on heating, it would seem that this method of determining water would give low results. But, excepting the normal alkaline tellurites, the oxidation is so slow that the error arising from this source would be imperceptible. Thus when anhydrous magnesium tellurite is heated to 450° for 15 hours, the gain in weight due to oxidation is only 0·25 per cent, and in 77 hours it is only 1·5 per cent. Again, nickel tellurite after being heated at 450° for 70 hours, contained only 0·46 per cent of active oxygen. In contrast with these long periods of heating, the length of time necessary to drive off all the water is only 15 minutes.

Summary.

1. The tellurites of the alkaline metals can be prepared by fusing together tellurium dioxide and a metallic oxide, hydroxide, or carbonate. Since, however, tellurous acid forms salts of different types, namely, the mono-, di-, and tetratellurites, the starting material must be used in definite proportions in order to obtain a tellurite of definite composition. The tellurites of the heavier metals are best prepared by double decomposition.

2. The alkaline tellurites are soluble, the alkaline earth tellurites are slightly soluble, and those of the heavy metals are insoluble.

3. As a class, the tellurites are unstable compounds. Tellurous acid is easily displaced at ordinary temperatures in presence of moisture by carbon dioxide.

4. The tellurites can be oxidised by heating in the air at a temperature of 440—470°. This oxidation is fairly rapid in the case of the normal alkaline tellurites.

5. The tellurites of most of the metals other than potassium and sodium, as well as the ditellurites of the alkali metals, oxidise when heated much more slowly than the normal alkaline tellurites.

6. In potassium ditellurite, only one-half of the tellurous acid is oxidisable by this means, forming the compound $K_2O.TeO_3.TeO_2$. The tetratellurites are not oxidisable by heating in the air at 450°, neither is pure tellurium dioxide.

7. Manganous tellurite will oxidise on contact with the air at the ordinary temperature, but in this case the manganese is oxidised, passing to the trivalent state.

8. Ammonium tellurite probably exists in solution, and also in the solid state when surrounded by a saturated solution of tellurous acid in ammonia, but otherwise decomposes spontaneously at the ordinary temperature, forming hydrated tellurium dioxide.

9. Silver tellurite can be obtained in a number of different varieties. When precipitated in presence of an excess of sodium tellurite, it is white, but when silver nitrate is in excess, the precipitate is of a pale yellow colour. This second form in the course of a few days turns to a bluish grey powder, while the first is stable. At 250° both turn to a deep purplish blue colour. Still, another variety can be obtained, by crystallising from an ammoniacal solution, as a deep brownish yellow substance. All of these forms are anhydrous.

10. The precipitated tellurites are all flocculent and amorphous, and with the exception of the magnesium salt, show practically no tendency to become crystalline.

11. These precipitates are very apt to occlude other salts as impurities, which are very difficult to remove. This tendency is most marked in the barium salt, which will occlude large quantities of barium chloride. In the case of lead tellurite, which was precipitated from a solution of lead nitrate, the precipitate contained nitrates, but these were not so difficult to remove as the chlorides.

12. With the exception of the silver salt, these precipitates are all definite hydrates, which do not readily give up their water.

THE PHYSIOLOGICAL PRINCIPLES OF HEATING AND VENTILATING.*

By Professor LEONARD HILL, M.D., F.R.S.

Lecture I.—The Qualities of Expired Air in Crowded and Confined Places.

Professor Leonard Hill began his lecture with a consideration of the atmosphere and its climatic variations, and the influence of the pressure of oxygen on life. In describing the mountain sickness which affects mountaineers and aeroplanists, when rapidly rising into the attenuated air of high altitudes where the pressure of oxygen has fallen from 21 per cent to 12 per cent of an atmosphere, he stated that the sickness is made worse by muscular effort, but instantly relieved by breathing oxygen, and he demonstrated the working of a very light portable apparatus for generating and inhaling oxygen. This apparatus is not, however, required by persons who live on heights, as the body quickly compensates for the lessened pressure of oxygen by concentration of the blood, and slowly by the formation of new red blood corpuscles. Those who dwell at high altitudes have less water and more red corpuscles and haemaphæbin in their blood. The lecturer also described the dangers to divers and caisson workers of breathing compressed air, which causes a solution of nitrogen gas in the watery fluids and the fat of the body. This gas may bubble off in the blood and disturb the circulation after the men have come out of the compressed air; but the danger can be prevented by proper methods of regulating the duration of work and the time of compression.

Passing to a consideration of the atmosphere of strictly confined places—sewers, wells, mines—the lecturer explained how de-oxygenated air collects, owing to the oxygen in the air being used up by the soil, and he demonstrated a second breathing apparatus by which rescue-work in de-oxygenated and irrespirable air is made pos-

* Chadwick Public Lectur s, Bristol, 1913. (Delivered at Bristol University, October 23. The Vice-Chancellor, Sir Isambard Owen, M.A., M.D., in the Chair).

sible. Explosions in coal mines, so Professor Hill stated, could be prevented, if the oxygen in the air were lowered from 21 to 17 per cent of an atmosphere, and this would have no deleterious effect on the miners. The great explosions of recent years are due to the improved ventila tion of mines.

The injurious effects of dust in the atmosphere were next dwelt upon. Lead-poisoning is due to inhalation of lead dust. Workers in silicated stones or metal suffer greatly from phthisis, and for these also there was shown an apparatus—simple in the working—by which fresh air can be blown over the mouths of workers in dusty trades.

Referring to the dust of the roads, the lecturer said every effort should be made to reduce it. Streets should be cleaned with water and not swept. Infection was certainly spread by dust, as also by insects and by the spraying of saliva in spitting, coughing, sneezing, and talking. Saliva spray is probably the chief cause of infection by common colds and phthisis. It is one which can be limited by training people to sneeze and cough into handerchiefs, and to speak, when infected with catarrh, into newspapers held in front of their faces.

Continuing the main discussion of his lecture, which was specifically on the qualities of expired air, Professor Leonard Hill said :—"It has generally been supposed that all the bad effects of close crowded places are due to chemical impurity of the air, that the air is contaminated by the exhalations of human beings, and that it becomes impoverished of oxygen. But what people always complain of is the heat and want of movement of the air." Proof lies that the excess of carbonic acid in the air in a crowded room if sufficient to have any effect at all will only make people breathe a little more deeply and ventilate their lungs more fully.

The oxygen in a crowded room is never diminished by more than 1 per cent, the cracks, crannies, and pores in the room always suffice to let fresh air in, so that the oxygen does not suffer a greater diminution. This diminution of oxygen has no physiological effect whatever. In the famous Alpine health resorts there is a greater diminution in the concentration of oxygen owing to the attenuation of the air at higher altitudes. Therefore the chemical state of the air, so far as regards carbonic acid and oxygen, has nothing whatever to do with the discomfort which is felt in crowded and confined places, or with the healthful effect of open-air life.

A great deal has been made of the supposed existence of volatile organic poison in expired air. Its existence is asserted in all the popular books of hygiene. There is no evidence, worth anything, in favour of the existence of this organic poison in expired air.

The unpleasant smell of crowded confined atmospheres are not smelt by the crowd within, but only by those who come in from the fresh air. There is no evidence that such smell has a poisonous effect, but it may nervously affect sensitive people, especially those who imagine it betokens the existence of a poison in the air ; the smell may be prevented by cleanliness of person, clothes, and habitations.

Conclusive evidence will be brought forward in the next lecture to show that the physical conditions of the atmosphere, heat humidity and movement, very greatly influence our comfort and health.

Binary System of Thallous Chloride with Chlorides of Divalent Metals.—C. Sandonnini.—Unlike potassium chloride, which it resembles in some respects, thallous chloride gives with lead and stannous chlorides at high temperatures solid solutions in all proportions. With mercury chloride two compounds are formed, $Tl.Cl.HgCl_2$ and $4TlCl.HgCl_2$ (?), the second of which was not known previously. With cadmium chloride thallous chloride gives only one compound, $TlCl.CdCl_2$, while with potassium chloride at a high temperature, in addition to the analogous compound, the compound $4KCl.CdCl_2$ is obtained.—*Atti Reale Accad. dei Lincei*, xxii., [ii.], No. 1.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

International Conference on the Metre.

The International Conference on the Metre has just opened at the Ministry of Commerce, under the presidency of Prof. Appell, Member of the Academy of Sciences. It has come to several important decisions ; first of all, the delegates have verified the standard kilogrms. of the different countries adhering to the convention of the metre. Only the Danish, Hungarian, and Servian kilogrms. have undergone important alterations. The kilogrms. of the other nations had not varied a hundred millionth of their weight, which would be a small error, equal to that which would be made if one made the mistake of the earth's meridian. The Conference has also decided that the States that possess geodesic bases shall exchange amongst themselves the Invar wires, so as to verify, very precisely, the length of these bases. Moreover, the standards with ends that are used to give the calibre to pieces of machinery will have a definition temperature equal to zero degrees. Thus in the whole world there will be one single scale for the construction of machinery. The Conference has foreseen the time when the temperature scales actually in use will be abandoned. The hydrogen thermometers are those by which low temperatures may be attained ; temperatures of $-252°$ to $-271°$, which is the temperature of the liquefaction of helium. Preparatory studies are soon to be undertaken in order to reach, in a near future, a scale of a still greater elasticity, that of thermodynamic temperatures.

Prehistoric Art.

In a Grotto situated near Poncin, at the spot called La Colombière (Ein), two *savants*, MM. L. Mayet and J. Pissot, have just discovered a bone of a mammoth engraved with a human face. When presenting their notice to the Academy, M. Donvilli indicated that this engraved bone was found in the upper auragnacian stratum. Our prehistoric ancestors have traced on this mammoth bone the profile of a man with a convex forehead, a very high face, lengthened by a beard, indicated by hatchings beneath the chin. The nose is long and full, the pilosity of the trunk is abundant. Above it is to be seen a female outline, representing only the middle part of the body.

The Total Cube of the Water of the Earth.

Professor W. Halbfass reckons that the total cube of water of the terrestrial globe is 1,304,068,550 cubic kilometres. The greater part of this volume, that is to say 1,300,000,000 cubic kilometres, is in the Oceans. Next in order of importance comes the quantity of water contained in the icy regions, especially the ice of the Poles, that is to say 3—5 millions of cubic kilometres. The lakes and ponds would contain 250,000 cubic kilometres, the sub terranean waters a similar quantity, the rivers 50,000 cubic kilometres, atmospheric water 12,300, the marshes 6000, and the snow on the surface of the ground 250,000 cubic kilometres. The total volume of the terresitrial globe being 1,083.205 millions of cubic kilometres, the volume of the waters is equal to 1/830 of the volume of the Earth.

A Cure for the Sleeping Sickness.

The researches of learned men concerning one of the most terrible diseases of the Black Continent, the sleeping sickness, have very much increased during the last few years, without, however, any definite result having been obtained. In a paper recently presented before the Academy of Sciences by M. Laveran, M. Danyez, of the Pasteur Institute, signals the fact that, in the treatment of trypanosomiasis, it is advantageous to make use of several medications, not one alone being sufficiently energetic to cure the disease. Thus, the simultaneous employment of several arsenical combinations, such as arsenious acid, orpiment, and atoxyle, gives very interesting results. M.

Danyez has tried to obtain a solution of arseno-benzol and nitrate of silver. This combination has had a very energetic action on animals attacked by trypanosomiasis. In *surra* and in trypanosomiasis occasioned by the spirilla of Rhodesia—the same microbe as that of the sleeping sickness—exceedingly remarkable results have been obtained with very small doses of arseno-benzol and nitrate of silver. A single injection of one-twentieth part of a milligrm. has sufficed to cure a mouse weighing 20 grms., and rabbits weighing 2 or 3 kilogrms. were cured by a single intra-venous muscular injection of 5 milligrms. of this new product.

NOTICES OF BOOKS.

Organic Chemistry for Advanced Students. Volume II. By Julius B. Cohen, Ph.D., B.Sc., F.R.S. London: Edward Arnold. 1913.

This is a valuable text-book of organic chemistry for advanced students, and if the author's suggestions as to the order in which the chapters are read are followed a good grasp of the fundamental principles and of the recent development of the subject should be acquired. A description of the details of the individual substances of organic chemistry is not given, but rather a general survey of the nature and dynamics of organic reactions, and such difficult subjects as the connection between molecular structure and the more important physical properties are excellently treated. Modern theories of the causes of colour and its connection with structure are discussed in a particularly interesting and up-to-date chapter. The book has an exceptionally high educational value, and it strikingly exemplifies the recent changes and improvements which methods of teaching organic chemistry have undergone.

A Systematic Course of Practical Science for Secondary and other Schools. Book II. *Experimental Heat.* By Arthur W. Mason, B.Sc., B.A. (Lond.). London: Rivingtons. 1913.

This book describes an excellent course of experimental work in Heat, and in all respects it is quite up to the high level of the first volume on Introductory Physical Measurements. Every effort is made to encourage the student's independence and self-reliance, and if he works carefully through the course he can hardly fail to become an accurate and exact worker. The book is intended for rather older pupils than the introductory course, and those who use it are supposed to have some knowledge of the best methods of recording results and describing experiments. The apparatus required is in all cases quite simple and the directions are very detailed and precise. Additional questions involving calculations are given in great abundance, and also some extra practical exercises. The importance of the use of graphical methods of representing results is emphasised, and by his questions and hints the author shows that he thoroughly understands the usual difficulties of the beginner, and knows exactly how to help him to find his own way out of them.

Brazil in 1912. By J. C. Oakenfull. London: Robert Atkinson, Ltd. 1913.

A glowing account of the resources and possibilities of Brazil is to be found in the fourth annual edition of this handbook. Intending settlers can derive from it much information about the laws, the state of education, the cost of living, salaries, &c., and the various industries, and the illustrations are a very attractive feature. The author is an enthusiastic believer in the successful future before Brazil, and his comments and advice to colonists appear to be apposite and worthy of careful attention.

On the Circulation of Energy and Matter. By Edward M. Darken. Wellington, New Zealand. 1913.

The author of this pamphlet believes that he has discovered the key to the solution of the problem of the origin of life, and he has worked out a theory of the formation of the living cell from a droplet of water by the force of suction. Matter itself he would regard as being made by the sun, which is "alive just as much as we are." He states his argument in a very condensed form, and makes many assertions which are at variance with commonly accepted opinions without bringing forward any proof of them. However, his speculations and reflections may possibly interest the somewhat limited public to whom they are addressed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 7, August 18, 1913.

Absorption Bands in Ultra-violet Spectrum of Alcohols of the Fatty Acids.—MM. Massol and Faucon.—The spectra of the two abnormal primary alcohols, 2-methyl-3-propanol-2-methyl-1-butanol and 2-methyl-4-butanol, show two absorption bands between λ 2500 and λ 2700, and λ 3060 and λ 3150. These two absorption bands are peculiar to these alcohols, and are not found in the fundamental hydrocarbon, nor in the other alcohols or their halogen derivatives. The aldehydes give a single broad band corresponding approximately to radiations intermediate between those of the two bands of the alcohol.

No. 8, August 25, 1913.

Isomerisation of $\beta\gamma$-Unsaturated-α-hydroxyl Acids to form γ-Ketone Acids.—J. Bougault.—By the action of acids of medium strength (oxalic or phosphoric) α-phenyl-oxycrotonic acid is partially transformed into γ-phenyl-oxycrotonic acid. Thus in all probability the transformation of the $\beta\gamma$-unsaturated α-hydroxyl acids into γ-ketone acids begins with the formation of $\alpha\beta$-unsaturated γ-hydroxyl acids and no other intermediate term is formed. The following formulæ show the changes that occur:—

$$R.CH.=CH.CHOH.CO_2H \rightarrow R.CHOH.CH=CH.CO_2H \rightarrow R.CO.CH_2.CH_2CO_2H.$$

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 15, 1913.

Relations of Isomorphism in the Organo-metallic Series.—Paul Pascal.—The thermic analysis of binary mixtures of the monohalogen derivatives of benzene shows that the four halogens can be divided into two groups. The first group consists of fluorine alone, which is different from any of the others, since benzyl fluoride always gives a eutectic when it is mixed with the homologous halogen derivatives. The other group contains chlorine, bromine, and iodine, which taken in pairs always give a continuous series of mixed crystals. Chlorine and bromine resemble one another more than they resemble iodine. These results agree with those obtained when the halogens are regarded from a chemical point of view. If mixtures of benzyl cyanide with the benzyl halogen derivatives are analysed by the thermic method it is found that the cyanogen group does not resemble the chlorine-bromine-iodine group.

Atti della Reale Accademia dei Lincei. Vol. xxii. [i.], No. 12, 1913.

Ortho-halogen Derivatives of Paranitroaniline.—G. Körner.—If paranitroaniline is dissolved in hydrochloric acid and chlorine or bromine is passed into the

solution, a mono or dihalogen derivative is readily obtained. Thus, if chlorine is introduced into the boiling solution in the proportion of one molecule to one molecule of the aniline derivative, orthochloro paranitroaniline is obtained, while at the ordinary temperature the dichloro-derivative is formed. The bromine compounds can be prepared similarly, and the iodine compounds by using iodine chloride. In the last case a mixture of the mono- and di-derivative is obtained, and may be separated into its constituents by treating with alcohol, in which their solubilities are very different.

Polyazoxy Compounds.—A. Angeli. – Bisazoxybenzene (melting-point, 155°) when treated with concentrated sulphuric acid at 100° gives two products, the formula of the first of which is undoubtedly $C_6H_5.N_2.C_6H_4.N_2.C_6H_4(OH)$. It furnishes an ethyl ether which fuses at 138°. When sulphuric acid acts on bisazoxybenzene at 0° two yellow products, both insoluble in alkalis, are formed, and a third, red product which is easily soluble in soda. The first of these is an isomer of the original substance, fusing at 168°. It is reduced by means of aluminium amalgam to Mills's bisazobenzene. The soluble product fuses at 148°, and appears to be a third isomer. These three isomers can probably be represented by the formulæ:—

α-Form,—

$$C_6H_5.N=N.C_6H_4.N=N.C_6H_5$$
$$\quad\quad\quad

THE CHEMICAL NEWS.

VOL. CVIII., No. 2815.

DETERMINATION OF MELTING-POINT BY THERMOMETER BULB METHOD.

By ROBERT MELDRUM.

THIS method of determining the melting-point of waxes, fatty acids, fats, and organic compounds in general is used extensively in analytical work, but frequently the results obtained have shown a wide variation in the melting-point in the same sample. This has given birth to the general opinion amongst analysts when dealing with solid fats and waxes that the melting-point is affected according to the prolonged melting and rapid cooling of the fat. After the thermometer has been coated with the substance it is generally assumed that a long interval of time must elapse, two, six, twelve, and even twenty-four hours, before the fat attains its normal condition. The accepted theory is that the fat, after being melted and solidified rapidly, has undergone molecular or physical changes which increase or decrease the melting point beyond the normal. That this theory persists extensively is shown by a great deal of the literature dealing with the melting-point and solidifying-point of fatty substances, where nearly, without exception, great reliance is placed in melting the fat a few degrees above its melting-point, and not for too long. The temperature at which the substance is melted, the time during which it remains melted, and the cooling down process have all become to be considered as important points connected with regularity in melting-point and solidifying-point determinations. Very little work has been done in the investigation of the rising and falling of the melting-point above normal, due to thermal and other physical conditions inherent in the heating and cooling. That the solidifying-point may go considerably beyond the normal when ultra conditions are present is seen in Deprez's experiment of cooling down water to $-20°$ C. without solidifying. But so far as the author's experience goes, extending over the past twenty years, and dealing with all classes of fatty matter, the variation in the thermometer bulb method of determining the melting-point is not due to the thermal treatment of the fat but to errors in manipulation. The following fats were melted and thermometer dippings made and placed aside for various intervals of time, and the melting-point taken, the same thermometer being used throughout :—

Mutton Tallow and Fatty Acids (o° C.).

	10 mins.	15 mins.	30 mins.	2 hrs.	16 hrs.
Mutton tallow	48·4 48·0 48·4		48·4	48·0	48·5
Fatty acids		47 6 47 6			47·8
	50·6 50·6 50·4				50·4
	38·8 38·8 39·0				39·0 39·2

The thermometers used for this method by various observers differ greatly in the size of bulb, and this has an important influence on the melting-point. When the bulb is small it is more sensitive to heat, in so far as it indicates changes in T° rapidly, whereas with the large bulb the changes are slower. With the large bulb the heating must be slower ; if too rapid the readings will be low. But this question of large and small bulb is easily decided in favour of the former, as then the coating of fat is directly on the bulb or at the point where the temperature is indicated. It is needless to say that in all melting-point determinations good thermometers must be used divided into one-tenth degree.

The most convenient apparatus for determining the melting-point by this method is a tall beaker, about 7 in. long by 3 in. diameter, to which is fitted a bung. A test-tube 7 in. by 1 in. is passed through the bung in the centre. A glass stirrer in the form of a plunger to work up and down the *outside* of tube is also fitted. The beaker is filled with water. The thermometer with its layer of melted fat is fixed centrally in the test-tube by means of a bung. During the heating the water must be kept in complete circulation.

The sample of fat, if containing moisture or suspended matter, must be filtered through hot water funnel containing several layers of filter-paper. The fat is melted at 10° above its melting-point, but the author has never found the melting-point of any fat to be altered when maintained at even 212° F. for eight hours, nor by repeated re-melting and solidifying. This is the last cause to be looked for in explanation of any variation in the melting-point.

The most important point connected with the manipulation is coating the bulb with the fat. When the melting-point of fat is high, if the thermometer is rapidly dipped in and out, the coating of fat will be thick, and when the melting-point is determined an opaque drop is likely to be formed with low results. If the cold thermometer is dipped into fat and allowed to remain for a few seconds and then withdrawn, the film of fat will be thin, only sufficient fat being on bulb to form a drop slowly and above the normal melting-point. On the other hand, with low melting mixtures, even with the thermometer cold and rapidly dipped in and out of fat, the coating is often too thin, and gives high readings. With these very soft mixtures it is essential to cool the bulb down to 0° or $-5°$ C. with ether or carbon bisulphide, and then to make a rapid dip. Some variation in the manipulation is required when dealing with some waxes and solid glycerides to obtain coatings of proper thickness. To ascertain when the coating is of proper thickness the author has been accustomed to melt the sample about 10° above its melting-point, and to make a rapid dip in and out, and cool for fifteen minutes, at 10° at least below its melting-point. When the melting-point is determined and if the first drop of fat that appears is opaque, the coating is too thick, and if the drop of fat hangs too long on the bulb, and if a second drop fails to appear, the coating is too thin. The thermometer is now cooled or heated 5° or 10°, as the case may be, and a rapid dip in and out made, and the melting-point again determined. Previous to determining melting-point the fat on apex of bulb ought to be removed by piece of filter-paper, otherwise the readings will be too high. Failure to remove the fat from apex will often result in erratic readings. In this way the T° to which the thermometer must either be heated or cooled is readily ascertained. Sufficient fat ought to be on the bulb to form two drops, as will be seen from the following examples :—

Mutton Tallow (o° C.).

First drop appears ..	48·4	48·0	48·4	48·0	48·5
First drop off	48·6	48·2	48·6	48·2	48·7
Second drop appears	48·7	48·4	48·8	48·3	48·9
Second drop off ..	48·8	48·6	49·0	48·6	49·1

Mutton Tallow Fatty Acids (o° C.).

First drop appears ..	47·6	47·8	47·8
First drop off	48·0	48·0	48·0
Second drop appears	48·2	48·2	48·1
Second drop off ..	48·4	48·5	48·2

The thickness of coating is of first importance. The thick coating acts as a heat insulator to the bulb, and requires extra slow heating to allow bulb to attain actual temperature of the fat. Moreover, due to these thick films, the flow to form a drop is quicker, forming globules of opaque and semi-melted fat. These opaque drops are really mixtures of solid and liquid fat, the viscosity of the mixture being higher than the liquid fat itself. The movement of these opaque drops depends on the mass of fat itself. When the viscosity of the molten fat is high, time is required to form a drop ; if the heating is too rapid a T°

above the actual melting-point is required to produce sufficient viscosity to flow.

This question of viscosity plays a very important part in all methods used for determining the melting-point. At the critical point, when a solid is changing into the liquid state, very high viscosity at this point results, which frequently cause enormous pear shaped drops to form, and which tenaciously hang to the bulb and then drop off as a semi-solid. Due to this cause some waxes and fats will form drops which fall as threads. With some mixtures the whole of the fat on the bulb will slip off before the actual melting-point is attained. It would therefore appear on these theoretical grounds that the melting-point by this method is too high, due entirely to the phenomena of viscosity and also to the change in density which takes place at the critical point. As is well known, the glycerides have a higher viscosity at all temperatures than their fatty acids, but with the solid glycerides, and no doubt wax alcohols, the viscosity at the critical point when the solids change into liquids must be so great that no flow will take place at the melting-point, but only at temperatures above same.

From these considerations it will be evident that as the melting-point is approached the speed of heating must be very slow to allow sufficient time for the drop to form. Two minutes per °C. is not too slow. Within 2° of the melting-point the author is accustomed to remove the source of heat for two to three minutes until the thermometer ceases to rise, and then apply the heat again, and when 0·5° C. from the melting-point, again removing the flame, and maintaining it at this for two to three minutes, and so on till the drop forms.

Forty-five determinations of various mixtures of stearic and oleic acid with melting-point varying from 32·8 to 55·8, the maximum variation was 0 6° C.

The following fifty-nine determinations as detailed below also show the maximum variation not to exceed 0·6° C.:—

Melting-point by Thermometer Bulb Method.

Materials.	Melting-point °C.					Diff.
Stearine	56·0	56·0				—
80 per cent stearine, 20 per cent mineral oil ..	53·0	52·8				0·2
60 per cent stearine, 40 per cent mineral oil ..	51·0	51·2				0·2
40 per cent stearine, 60 per cent mineral oil ..	45·8	46·1				0·3
20 per cent stearine, 80 per cent mineral oil ..	39·8	40·4				0·6
Mutton tallow	48 3	48·2	48·4	48·4		0·2
Mutton tallow acids ..	46·8	46·8	47·0			0·2
Mutton tallow	48·4	48·0	48·4	48·0	48·5	0·5
Mutton tallow acids ..	47·6	47·8	47 8			0·2
Mutton tallow	50 0	50 0	50 6	50·3		0 6
Mutton tallow acids ..	49 8	50·0	50·0	49·8		0·2
Beef tallow	46 6	46·3				0·3
Beef tallow acids	43·8	44·0	43·6			0·4
90 mutton tallow, 10 hard oil	48·0	47·6	47·8	48 3		0·5
80 mutton tallow, 20 hard oil	47·4	47·2	47·6	47·4		0·4
Stearine	55·8	55·4	55·6	55·6	55·4	0·4
20 stearine, 80 oleic acid	32·8	33·0	33·2	33·4	33·2	0·6
Spermaceti	45·3	45·3	45·4			0·1

Time has not been available to investigate other methods of determining the melting-point, and how far these compare in accuracy with the thermometer bulb method. Nor has the author determined how far the results obtained by this method agree with the actual melting-point. This would require an enormous amount of labour. With stearic acid the melting-point is about 0·8° C. higher than the solidifying-point, whereas with spermaceti the melting-point is 0·4° C. lower than the solidifying-point. It has also been shown (CHEMICAL NEWS, cviii., 199) that the difference between the solidifying-point and melting-point of mixtures of stearic and oleic acid decreases and then increases as the softness increases. With tallows the difference between the solidifying-point and melting-point by this method amounts to 8° C. So far as the comparatively pure substances, stearic acid and spermaceti, are concerned the thermometer bulb method apparently yields results well within 1° C. of the true melting-point. This statement also holds good for mixtures of stearic and oleic acid up to 60 per cent oleic.

AN APPARATUS FOR THE PURIFICATION OF MERCURY BY DISTILLATION IN A VACUUM.

By BERTRAM LAMBERT.

THE apparatus described below has been used very successfully for the purification of large quantities of mercury. It is simple in construction, rapid in action, and does not require any pump for exhausting it before use.

The figure shows the essential glass parts of the apparatus, which should be mounted firmly on a stand with some provision made for adjusting the height of the vessel M (see fig.).

The bulb A is of about 300 cc. capacity, and has a wide tube, B, sealed through its upper end as shown in the figure. This tube B is provided with a well-fitting rubber stopper, through which a narrow tube, D, passes to the bottom, and also with a side-tube, E. The lower half of the tube B should be thin-walled, and should be tapered slightly towards the closed end. This tube acts as a water cooled condenser for the mercury vapour, and the efficiency of the apparatus is greatly increased by having it as large as possible, and also as thin in the wall as is consistent with strength. A side-tube, F, is sealed into the bulb quite close to the junction between A and B. This tube should be bent up very steeply and drawn out to a capillary at the upper end.

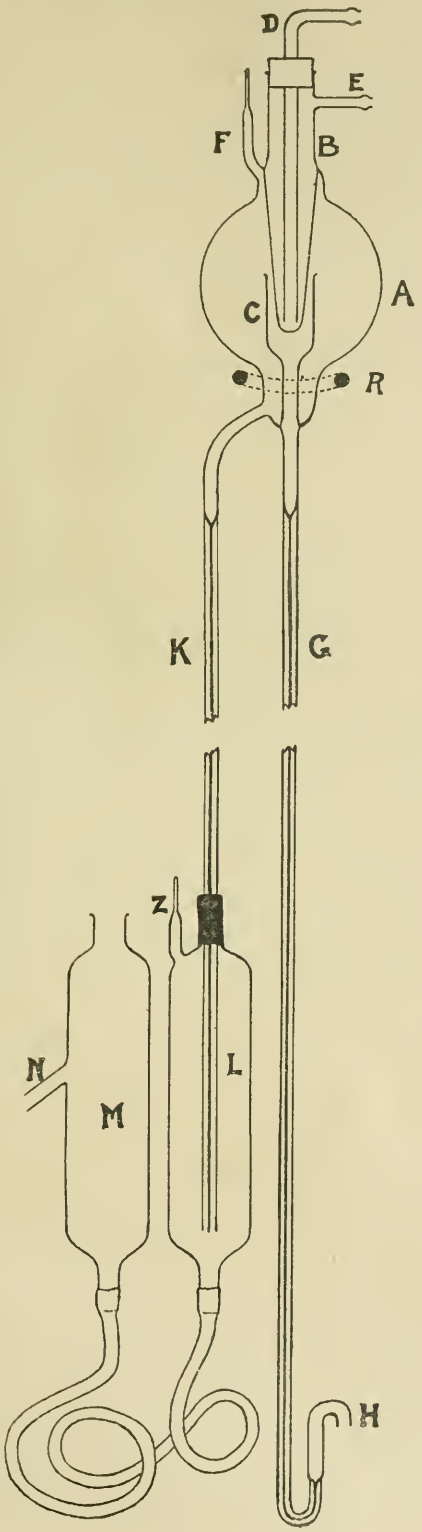
Into the lower end of the bulb is sealed a tube, G, which is widened out into a cup, C, at the top as shown in the figure. This cup is arranged so that its rim is just above the middle of the bulb A, the lower end of the condenser B being made to project about 3 cm. into it.

A side-tube, K, is sealed into the lower part of the bulb and bent, as shown in the figure, parallel to G. The lower parts of these tubes K and G are made from capillary tubing with a bore of about 1 mm. A wider piece of tubing is sealed on the end of G, which is bent as shown in the figure. The length from G to H should be about 760 mm.

The tube K is made to slide through the neck of the vessel L, and a good air-tight junction is made at the neck by means of stout rubber tubing. The vessel L, which is about 300 cc. capacity, is connected with a similar vessel, M, by means of a long piece of canvas-lined pressure-tubing. M is furnished with a side-tube, N, the use of which is described below.

The length from the middle of the bulb A to the middle of L should be about 760 mm.

Mercury is poured into M until M and L are about two-thirds full. It is convenient to have a drawn-out side-tube, Z, in the vessel L so that the air pressure can be adjusted during this operation. After the operation the point of Z is sealed. By raising M the mercury is made to rise slowly into the bulb A. It overflows into the cup C, and in order to prevent the escape of the mercury through G, the end H must be closed with a rubber cork. M is now raised further so that the mercury fills the bulb completely and rises into the drawn-out portion of the tube F. Care should be taken that no air-bubbles are trapped in any part of the bulb or cup. The capillary of F is now carefully sealed, while it is full of mercury, and the reservoir M is then gently lowered. The position of the reservoir M is adjusted so that the level of the mercury in the bulb A is about 5 mm. below the rim of the cup C. The point of the tube Z is



then cut off so that the air in L is kept at atmospheric pressure. A jar is now placed below H and the rubber cap removed. The mercury flows out from the cup C, displacing the air in the capillary G, and finally the difference in level between the mercury at G and H is the barometric height. If dry mercury has been used, and the above operations performed carefully, a very high vacuum will have been produced in the space above the mercury in the bulb.

Cold water is now made to flow through the condenser and the bulb heated, very gently at first, by means of a small ring-burner which is arranged as shown in the figure at R. An asbestos hood must be arranged round the bulb to protect it from draughts.

The mercury vapourises, is condensed on the cold tube B, and drops down into the capillary G. When sufficient mercury has been distilled to displace the mercury originally in G, the pure product can be collected. The drops of mercury falling into the capillary G act on the principle of the Sprengel pump, and maintain a very high vacuum in the bulb, removing the traces of air which enter the bulb dissolved in the mercury, and are then set free during the process of distillation.

The level of the mercury in the bulb will change with atmospheric pressure, and should be adjusted by altering the position of M. When the apparatus is working, mercury should be delivered into M through a fine jet at a rather faster rate than the mercury is distilling; by this means the level of mercury will be maintained in the bulb, the excess being collected at the overflow tube N. The apparatus can then be left working, without attention, for several hours.

The whole apparatus can be made from ordinary soft glass, and, if used carefully, will last many years. Care should be taken to heat the bulb gently, especially at first, and the flames from the burner should not be allowed to come into actual contact with the glass. Under such circumstances mercury can be distilled in the apparatus at the rate of about 3 lbs. per hour. The yield could probably be much increased by having the apparatus made from Jena glass or quartz and using a higher temperature, but there is no particular advantage to be gained. The purest product is got by slow distillation at as low a temperature as possible.

Mercury should be cleaned, by the usual methods, with 5 per cent nitric acid and thoroughly dried before distillation in the apparatus.

An extremely pure product may be obtained by frequent re-distillation, the apparatus being cleaned, washed, and dried between each operation.

The apparatus may be obtained from Messrs. A. Gallenkamp and Co., Ltd., Sun Street, Finsbury Square, E.C.

Chemical Department,
University Museum, Oxford.

INVESTIGATION OF MOLECULAR FORCES BY DISTURBANCE OF MOLECULAR EQUILIBRIUM IN LIQUID CRYSTALS.

By O. LEHMANN.

A SUBSTANCE is liquid if its elastic limit is zero, *i.e.*, if it cannot lastingly endure even the smallest elastic tension. There are many difficulties in the way of the practical determination of the elastic limit. The best method is as follows:—A plate of the substance under investigation is floated on mercury in a circular iron dish, in the middle of which there is a movable cylinder. The plate is attached to the walls of the dish and to the cylinder. The latter is caused to rotate by means of a string which is pulled with a force K. Equidistant radii are drawn on the plate. Within a certain circle of radius ρ the shearing force exceeds the elastic limit, and after a time it will be found

that within this circle the radii will be bent to form spirals, the effect being greater the longer the experiment lasts, while outside the circle there is only a very slight bending, which moreover disappears when K is removed.

As K is increased ρ also increases approximately proportionally, so that the graphic representation of the relation between ρ and K is a straight line through the origin, which however does not begin at the origin, but at a distance v from the K axis, if v is the radius of the cylinder. If $\rho = v$ the tension of the string is equal to the elastic limit, which may be denoted by K.

If we use an amorphous bituminous substance, the consistency of which decreases as the temperature rises, the graphic representations are straight lines which are more nearly perpendicular to the K axis the higher the temperature, corresponding to lower values of the elastic limit, which becomes zero at the temperature of liquefaction.

The actual performance of the experiment is rendered difficult by the fact that the temperature in the available space shows great variations, so that it is impossible to get a sharp demarcation between the region of perfectly elastic and that of persisting deformation. Other reasons may make such an experimental determination impossible, viz., the complicated composition of the bituminous mass, and the rarefaction of the mass, caused by tensile stress, in the neighbourhood of the circle ρ and its condensation in the neighbourhood of v.

It is still more difficult to investigate the existence of an elastic limit in crystalline substances in which the possibility of plastic deformation has been denied. I first observed true plastic deformation in ammonium nitrate, the five solid modifications of which are softer the higher the temperature limits of their existence. From the graphic representations of the values of ρ it appears that the regular modification possesses no elastic limit, and that hence its crystals are not to be regarded as solid, but liquid.

It can easily be ascertained whether the substance is really crystalline or amorphous by allowing it to separate from a melt or solution. Only in the first case would single (anisotropic) individuals separate, which would grow and finally on coming into contact appear as fields of different orientation. On account of the difficulties already mentioned, it is usually impossible to determine whether the elastic limit of such a crystalline mass is zero.

In certain cases, however, these difficulties can be avoided, inasmuch as it is not necessary to carry out the experiments, but it may be deduced from the appearance of spontaneous homeotropism that the elastic limit must be zero. This spontaneous homeotropism is due to the replacement of the structure containing fields of different orientation by a simple anisotropic structure.

This process cannot be explained on the assumption that matter is continuous; it is a proof of the molecular hypothesis, and is moreover a new physical fact which cannot be deduced from existing molecular hypotheses, and demands an extension of them.

Spontaneous homeotropism excludes the existence of an elastic limit, for the elastic reaction force is caused by the molecules being distorted or pushed out of their position of equilibrium. Spontaneous homeotropism does not allow of the possibility of such an alteration of structure. If it occurred at a certain definite moment it would at once disappear (in consequence of spontaneous homeotropism) and the molecules would again become parallel of their own accord, and the cause of elastic reaction would thus be removed. It can be said with certainty that the confluent crystals of neutral ammonium oleate hydrate have no elastic limit and are liquid crystals.

It must be admitted that these liquid crystals have not a uniform structure like the model crystals of mineralogical collections. If even they possess a uniform structure at the moment of their formation, as is not improbable, inasmuch as the external form shows the existence of a dual axis of symmetry, this structure must be lost when they flow together. Hence I conclude that the individuals formed on flowing together no longer possess a dual axis of symmetry but a circular cross-section, and that they behave as if they consisted of leaflet shaped molecules (perpendicular to the optical axis), the surfaces of which readily become parallel to one another, while their edges are not parallel. Perhaps thermic movement is sufficient to make the orientation of the edges irregular and constantly changing, while it cannot prevent the surfaces remaining parallel. This molecular arrangement I called semi-isotropic (formerly pseudo-isotropic) because it is midway between the ordinary grating structure of solid crystals and the quite irregular molecular arrangement in amorphous liquids.

This semi-isotropic structure is homogeneous only in the case of relatively small individuals. Various discontinuities appear in larger masses, and the molecules arrange themselves so as to give rise to the formation of twin structures or fan structures.

All these structures, both homogeneous and discontinuous, are stable positions of equilibrium of the molecules, for they are re-established after disturbance by external forces. If thermodynamics (or rather the kinetic theory) did not require a continual energetic movement of the molecules, which cannot yet be demonstrated in liquid crystals by the Brownian movement of fine particles floating in them, we should imagine a state of static equilibrium of the molecules under the influence of electrostatic and electrodynamic forces. The difference between solid and liquid crystals must then depend upon the fact that in the latter the molecules can wander from place to place under the influence of thermic motion (if inequalities of this movement occur, such as are necessary for diffusion), while this is not possible for solid crystals, or at any rate not unless a strain exceeding the elastic limit is exerted on them.

In the latter case, for example, when a prismatic crystal is bent, the wandering of the molecules causes the decrease (relaxation) of the elastic tension, and the grating structure is destroyed. When a liquid crystal of ammonium oleate is bent in consequence of spontaneous homeotropism the elastic tension disappears completely and the structure becomes fan-like. A state of perfect molecular equilibrium is not reached, for such bent liquid crystals are only observed momentarily, where the hydrodynamic force compels them to follow curved lines of flux, or where they become attached to the glass. When floating freely they spontaneously assume their normal form, like each fragment resulting from the destruction of an individual. With liquid crystals the equilibrium of the molecules extends not only to the structure but also the form. It is doubtful whether capillary pressure and expansive force come into play, and there is much uncertainty about the nature of molecular equilibrium and the forces which condition it. It seems to me that the first task of molecular physics is to examine the nature and action of these forces. The same method which was used for non-molecular forces, the disturbance of the state of equilibrium by known external forces, may lead to the desired result.

A case of this kind is the disturbance of molecular equilibrium by mechanical forces. If the plate in the torsion apparatus previously described were a liquid crystalline mass, and the rotation of the cylinder exceeded a certain speed, in accordance with previous observations of induced homeotropy, the axes of the molecules in the neighbourhood of the cylinder would all become parallel to the axis of rotation. Thus in a ring-shaped region a semi-isotropic structure would be established, the direction of the optical axis coinciding with that of the axis of the cylinder. The molecules behave like furniture castors, the axes about which they turn most easily being perpendicular to the direction of push. And just as on pushing a wheelbarrow fitted with castors the resistance to pushing decreases as soon as the castors have arranged themselves properly, the disc-shaped molecules, when arranged parallel to the plane of rotation, act like friction wheels so that the internal friction is lowered. The limit

of the semi-isotropic region is the place where the shearing force exceeds the molecular directing force. The latter can be ascertained by quantitative experiments of this kind.

By pressing the liquid crystalline mass between two glass plates the optical axes are made parallel to the glass, *i.e.*, the surfaces of the molecular leaflets are parallel to the glass. In very thin layers, or in narrow capillary tubes, the adsorption power of the glass acts in the same way. If the mass is made to flow through such tubes at moderate velocities, the interference bands remain unchanged in polarised light. Hence we may deduce that the molecules cannot be little rods, for then, since the rate of flow is greater round the axis of the tube than near the walls, they would arrange themselves obliquely if they were originally perpendicular to the glass. Leaflets, on the contrary, would easily glide over one another without losing their parallelism. As a matter of fact, a liquid crystalline mass between two glass plates can be made semi-isotropic in such a way that the optical axes are perpendicular to the glass while the plates are slowly pushed over one another. If the rate of flow in the capillary is greater in the neighbourhood of the axis forced, homeotropism must appear, the axes of the molecules turning through 90°. Here, also, quantitative experiments would give the molecular directive force.

Another case of the disturbance of molecular equilibrium is that caused by contiguous anisotropic plates, but here the acting force is not known.

Observations of the disturbance of equilibrium by magnetic forces which could easily be graduated would be of special value. Powerful surface tensions, such as for example appear at the surface of liquid crystals and air, might also disturb the arrangement of the molecules, in that they would compel the molecular leaflets to arrange themselves parallel to the surface. As the surface tension towards the mother-liquor is readily altered by suitable additions, there is a possibility of quantitative determinations. The most striking case is that of disturbances of molecular equilibrium by foreign substances which can form mixed crystals with the liquid crystals, and also the cases of swelling up in water and other liquids. The growth of myelin forms (of crystals of neutral ammonium oleate hydrate rich in water) and the apparently living crystals of parazoxycinnamic acid ethyl ester from monobromnaphthalene (which contain solvent) depend upon the same phenomenon. The direct cause is partly decrease of capillary pressure where the swelling up occurs and partly the crystallisation force.—Abridged from *Verhandlungen der Deutschen Physikalischen Gesellschaft*, xv., No. 10.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

Elements.—A very complete investigation of the precipitation of silver on glass in mirror form has been made by Kohlschütter (*Ann.*, cclxxxvii., 86). The solution used was ammoniacal silver nitrate with some reducing agent such as formaldehyde, grape sugar, milk sugar, tartaric acid, hydrazine, and others. In the solution very little silver is present as $Ag+$, but there is a relatively large number of $OH-$ ions. The precipitation of silver in mirror form depends upon the very slow oxidation of the reducing agent, silver oxide being the oxidising agent, and the concomitant formation of substances of high molecular weight or of colloidal form, everything which antagonises sol-formation being unfavourable to mirror formation. The character of the mirror is greatly influenced by the composition of the silvering solution and also by the character of the glass upon which the mirror is precipitated. The reason for the precipitation of the silver on the glass is that the silver hydroxide is adsorbed by the glass (hence the influence of the kind of glass), and the reducing agent must also be adsorbed by the glass. Thus everything that affects the surface tension of the solution affects the mirror. Microscopic and ultramicroscopic examination shows that the silver is amorphous and homogeneous, and it may be considered to be in a state of colloidal division. Thus while the mirror is unchanged by alkalis, it is easily removed by very dilute acids, though not dissolved. The sudden appearance of electrical conductivity in the mirror and its rapid increase are explained by the precipitate being laid down in discrete particles which in time bridge over the intervening spaces. The increase in conductivity of the finished mirror corresponds to the spontaneous coagulation of a metal-sol, while the increase under the influence of acids corresponds to the electrolytic precipitation of the sol. The mirror formed by the cathodic dusting of silver in dilute gases varies in character with the gas used, as does the precipitated mirror with the solution.

The rapidly increasing use of many of the rarer metals has led to fuller investigation of their properties. Efforts to get a pure vanadium have been made by Ruff and Martin (*Zeit. Angew. Chem.*, xxv., 49), but without complete success. Previous attempts to reduce the easily fusible V_2O_5 to metal having been unsuccessful. V_2O_3, which fuses at 2000°, was reduced by aluminum, as well as by carbon and vanadium carbide. The best product obtained was nearly 99 per cent pure. The difficulty of getting a pure metal lies in the fact that the vanadium dissolves the oxide VO, as well as aluminium and carbon, hence no latitude in proportion of reducing material is permissible, and the whole mass must react uniformly, conditions practically impossible of attainment. The melting-point of the pure metal was calculated as 1715° and the density as 5·688. Brunck (*Chem. Ztg.*, xxxvi., 1233) suggests the use of tantalum as material for electrodes, especially for analytical purposes. For cathodes tantalum can only replace platinum, being lighter, firmer, insoluble in aqua regia, without tendency to alloy with zinc and cadmium, cheaper, and is not attacked in the electrolysis of alkalis. Alone, it cannot be used for anodes, as it quickly becomes coated with a very thin but non-conducting layer of oxide (probably Ta_2O_4), but tantalum anodes which are very thinly plated with platinum serve every purpose. Tantalum has also been suggested as a superior material to platinum for accurate weights. Ruder (*Journ. Am. Chem. Soc.*, xxxiv., 387) has described the solubilities of malleable tungsten and molybdenum, and finds the former very slightly attacked by any acids or alkalis in solutions, though dissolved by fused alkalis. A saturated solution of sodium hypochlorite attacks it slowly and it is dissolved by a mixture of nitric and hydrofluoric acids, but not by chromic acid mixture. Molybdenum, on the other hand, presents little resistance except to hydrofluoric acid and alkali solutions. It is more readily dissolved by dilute than by strong acids. In a paper before the Section of Electrochemistry at the Congress of Applied Chemistry the properties and applications of ductile tungsten are very fully described. Among possible laboratory applications in replacing platinum are resistance furnaces, filtering gauze, acid-proof dishes and tubes, and analytical weights. The volatility of the metals of the platinum group, under conditions which appertain in the analytical laboratory, has been studied by Sir William Crookes (*Proc. Roy. Soc. London*, (A) lxxxvi., 461) using an electric resistance furnace as a source of heat. At 900° platinum is not volatile, but at 1300° it loses in two hours 0·019 per cent and in thirty hours 0·245 per cent. This would mean a loss of weight of 24 5 mgrm. from a 10 grm. crucible. The loss is due to sublimation, the sublimed metal being deposited in hexagonal flakes with metallic lustre. Iridium proves to be decidedly more volatile, losing 0·030 per cent in two hours and 0·092 per cent in twenty-two hours at 900°, while at 1300° the loss in two hours is 0·828 per cent and in twenty-two hours 7·297 per cent. Between 100° and 1400° the loss is pro-

* *Journal of the American Chemical Society*, xxxv., No. 2.

portional to the temperature. The loss is due to the formation of a volatile oxide. Rhodium suffers no change in weight at 900°, even after eight hours heating, and at 1300° loses but 0·021 per cent in four hours and 0·131 per cent in thirty hours. It is thus the least volatile of the metals of the group. Ruthenium at 1300° loses 25 per cent of its weight in eight hours, and this is attributable to the formation of an oxide. The reviewer may add that on heating ruthenium in a current of air in an ordinary combustion furnace the odour of RuO_4 is very distinct, and a lower oxide sublimes on the inside of the tube and on the porcelain boat containing the metal. The boiling-point of a number of metals at atmospheric pressure has been obtained by Greenwood (*Zeit. Elektrochem.*, xviii., 319), using a carbon crucible hung in a carbon tube which served for electrical heating, and determining the temperature of distinct boiling by a Wanner pyrometer. For those metals which are attacked by carbon a graphite crucible with fused magnesia lining was used. The following boiling-points were found:—

Mg 1120° Sb 1440° Al 1800° Ag 1955° Sn 2275° Fe 2450° Bi 1420° Pb 1525° Mn 1900° Cr 2200° Cu 2310°

The boiling-point curves for other pressures are shown in curves but the figures are not given.

The action of metals on fused alkalis has been continued by LeBlanc and Weyl (*Ber.*, xlv., 2300), and the results obtained with potassium hydroxide are found to be in many respects very different from those with sodium hydroxide. While sodium decomposes NaOH quantitatively at 450° with evolution of H and formation of Na_2O, K is without action on KOH even at 550°. When Na acts on KOH there is weak evolution of H, and K volatilises. With K on NaOH some H is given off but no metal. Evidently an equilibrium, $K + NaOH \rightleftharpoons Na + KOH$, is soon attained and then the Na acts on the NaOH. Al has no action on KOH, but it acts on NaOH moderately with evolution of H and H_2O. Cr, Mo, and W act on KOH slowly with evolution of H and formation of chromates, molybdates, and tungstates and some evolution of K. The reactions appear to be—

$$6KOH + M = M(OH)_6 + 6K,$$
$$M(OH)_6 + 2KOH = K_2MO_4 + 4H_2O,$$
$$4H_2O + 4K = 4KOH + 2H_2.$$

With C there is evolution of H, formation of K_2CO_3 and some K. The K appears to have no action on the K_2CO_3. With Mg there is evolution of H with KOH and precipitation of MgO, while with NaOH, Mg gives off both H and H_2O. With Si the reaction is violent and the formation of SiO_2 quantitative, but the H given off is somewhat less than the expected 4H for each atom of Si. With Ni, Co, and Fe there is no evolution of H or H_2O from KOH (as there is from NaOH), but the metals are attacked with the formation of a small amount of oxide. In general KOH is much more stable than NaOH.

In 1910 it was found by von Bolton that hydrocarbons were reduced by alkali-amalgams to carbon, a part of which appeared to be in the form of diamond. Utilising the fact that crystallising substances have a strong tendency to be deposited on crystals of the same substance if present, von Bolton (*Zeit. Elektrochem*, xvii., 971) led moist illuminating gas for four weeks through 14 per cent sodium amalgam in a tube coated with a very fine suspension of diamond powder in water-glass. The whole was kept at 100°. Under the microscope the powder was apparently amorphous, but after the experiment minute crystals were clearly visible. These showed the properties of diamonds, and while the quantity did not suffice for quantitative analysis it seems extremely probable that diamonds are thus formed by the reduction of hydrocarbons. Two important papers on ozone have appeared during the year, one by Harries (*Ber.*, xlv., 936) and one by Traube (*Ibid.*, 2201). The former finds that by the action of ozone on symmetrical butylene four products may be formed. When the ozone has been previously led through NaOH and H_2SO_4, there are formed a monomeric ozonide, $C_4H_8.O_3$, which can be distilled in a vacuum, and a dimeric form, $(C_4H_8.O_3)_2$, which is not volatile. If the ozone is not previously purified, two similar products are obtained but with the formulæ $C_4H_8.O_4$ and $(C_4H_8.O_4)_2$, which Harries calls oxozonides. Similar products are formed with other hydrocarbons containing a double bond. From these experiments Harries concludes that ordinary 11—14 per cent ozone is made up of about two-thirds ozone, O_3, and one-third oxozone, O_4, and that the latter is largely destroyed by leading it through alkali and acid, though the purified ozone still contains a little oxozone. Traube's experiments deal with the action of ozone on solid KOH. A red compound is formed which resembles in appearance $K_2Cr_2O_7$, and which decomposes in water or acids, giving off oxygen, chiefly as O_2, but with some O_3, while the solution contains some H_2O_2. On standing or heating, this red compound loses its colour and the white product decomposes with formation of H_2O_2 and evolution of oxygen. It is evident that the red product is a higher oxide, probably K_2O_7, which Traube calls potassium ozonate, but it contains some proportion of a lower oxide and also unchanged KOH. The oxide which is present with it and into which it decomposes on standing is doubtless the tetroxide, K_2O_4, since like this it gives H_2O_2 and oxygen in approximately molecular proportions. As Traube's ozone was passed over concentrated H_2SO_4 before absorption, no evidence appeared of the presence of oxozone.

The possible action of pressure in causing chemical reactions in the metamorphosis of minerals was several years ago suggested by Van Hise, and this has led to an experimental examination of the subject by Spezia (*Atti Accad. Sci. Torino*, xlvi., 19). By using pressures of 6000 to 9500 atmospheres, corresponding to depths of 20 to 30 kilometres, and in some cases continuing the pressure for several months, no instance of chemical action could be found. No action took place between silica and calcite, indicating no silicification. Alabaster, alum, and limonite, embedded in pulverised quartz for eight months at a uniform pressure of 8000 atmospheres, showed no loss of water. The great difference between the action of heat and of pressure was shown by the fact that goethite, heated in water to 330° for seven days, became anhydrous, while it remained unchanged under 9500 atmospheres pressure continued for twenty-six days. To test reduction, CuO was kept in contact with magnesium and then with potassium for months at 9500 atmospheres pressure without change, although the sum of molecular volumes would have been decreased by a reaction; nor was calcite changed to arragonite. Bismuth was not liquefied by a pressure of 9000 atmospheres. *A propos* of plasticity under pressure, Spezia calls attention to the great difference between one-sided pressure and a pressure uniform on all sides; the latter alone cannot liquefy metals nor plastic substances.

Bergius (*Zeit. Elektrochem.*, xviii., 660), working on reactions under pressure, finds that when peat is heated in water to 250—350° it is charred, and from the velocity of the reaction he considers it possible to calculate the time necessary for bituminous coal formation in nature. His calculations place the time at seven to eight million years, which he considers agrees with geological estimates.

Group II.—According to Bleyer and Müller (*Zeit. Anorg. Chem.*, lxxv., 285) from the chemical nature of glucinum it would be expected that compounds of glucinum and arsenic acid would be strongly hydrolysed, yet that in them the glucinum and the acid would be in a definite molecular ratio. This was confirmed experimentally, and tri-glucinum salts obtained when the di-glucinum would be normal, and basic salts where tri-glucinum would be called for. Thus disodium arsenate precipitated tri-glucinum arsenate from glucinum

sulphate, and trisodium arsenate a monobasic salt, $Gl_3(AsO_4)_2\,GlO.8H_2O$. Monoglucinum arsenate, $Gl(H_2AsO_4)_2$ and the di-glucinum salt, $GlHAsO_4$, were prepared by dissolving the calculated quantity of glucinum hydroxide in arsenic acid. The ammonium salt, $NH_4GlAsO_4.4{\cdot}5H_2O$ was fairly stable but the other alkali salts were basic, and the hydrolysis became greater on allowing the salt to stand in its mother-liquor. Except the monoglucinum arsenate, which consisted of hygroscopic crystal-flakes, all the compounds were amorphous. The behaviour of glucinum with arsenic acid seems thus to be somewhat similar to that with phosphoric acid, though the glucinum phosphates have not been worked out with sufficient definiteness to show a clear analogy.

(To be continued).

A STUDY OF CERTAIN CONFIRMATORY TESTS FOR TIN.

By LOUIS J. CURTMAN and MAX MOSHER.

I. *The Iron Nail Reduction Test followed by Treatment with Mercuric Chloride.*—This well-known test for tin, which consists in reducing the stannic chloride in acid solution with iron and subsequently treating the stannous chloride formed with mercuric chloride, was proposed by A. H. Allen in 1872 (*Journ. Chem. Soc.*, xxv., 274). It is mentioned in nearly every text-book on qualitative analysis. Despite its general use, nothing very definite appears to be known concerning the conditions under which this test may be relied upon to give constant results. The frequent failure of students to report this metal indicated the need for further investigation. It was therefore the object of this work to ascertain the best conditions for this test, and also to determine its limit under these discovered conditions.

The standard solution employed throughout this work was prepared in the following manner:—Ten grms. of chemically pure tin foil were treated in a 500 cc. Erlenmeyer flask with an excess of hydrochloric acid (sp. gr. 1·19), and solution was hastened by heating on a steam-bath. The solution was saturated with chlorine to completely oxidise the tin to the stannic condition. It was then boiled for some time to expel the last traces of free chlorine as well as to reduce the quantity of hydrochloric acid present. After cooling, the solution was diluted to 500 cc. in a volumetric flask. A portion, thoroughly mixed, failed to react with a saturated mercuric chloride solution, showing that all the tin was completely oxidised.

To determine whether any stannic chloride had been lost by volatilisation while the excess of chlorine was being boiled off, the solution was analysed for tin by the method given by Treadwell ("Quant. Anal.," trans. by W. T. Hall, p. 243). Two well agreeing determinations made on 20 cc. portions of the solution gave as the average result 19·9 mgrms. Sn in 1 cc.

To determine the quantity of free hydrochloric acid in the solution, separate portions of it were titrated with standard potassium hydroxide solution, by the method described by Treadwell (*Ibid.*, p. 495). The acidity was found to be 0·0063 grm. of anhydrous hydrochloric acid per cc., which, in the diluted solutions used in the tests, was reduced to such an extent as to be neglected without any appreciable error (Note 1).

This solution was not used directly, but 100 cc. of it were diluted with an equal quantity of water, giving a solution of 9·95 mgrms. Sn in 1 cc. In nearly all the sets of experiments performed the largest volume used was 0·5 cc., equivalent to 4·97 mgrms. Sn. This is practically 5 mgrms. Sn, and was so assumed in all experiments, for the reason that the error resulting from this assumption is too small to be detected by this test, as will be shown later. The smallest volume of this solution used was 0·1 cc. containing 0·995 mgrm. Sn, which for the reason stated above was considered 1 mgrm. When smaller quantities of tin were required, a portion of the second solution was again diluted so that 1 cc. was equivalent to 0·1 mgrm. Sn. In this dilution it was found that hydrolysis took place very rapidly; to prevent this, a new solution of similar strength was prepared, to which was added 5 cc. of concentrated hydrochloric acid to every 50 cc. (Note 2). This proved to be satisfactory.

The general procedure was as follows:—To definite amounts of concentrated hydrochloric acid pipetted into test-tubes were added varying quantities of a standard tin solution. After dilution to 5 cc. one or two nails were added, the tubes placed in a boiling water-bath (Note 3), and the reduction was allowed to continue for from two to five minutes; the contents of the test-tubes were then immediately filtered into 2 cc. of saturated mercuric chloride solution. The filtrates were examined after five minutes and the results recorded. In all cases where less than 1 mgrm. of tin was used the results were controlled by one, two, or even three blanks. This was necessary because it was found that under certain conditions a cloudy filtrate was obtained from the blanks. To determine whether this cloudiness in the blank was due to an interaction between a substance resulting from the action of the acid on the iron and the mercuric chloride, the following experiments were performed:—In separate test-tubes, one, two, and three 1½-inch cut nails were heated for five minutes with 5 cc. of hydrochloric acid (1—1) in the boiling water-bath, and the solution was then filtered into distilled water. The water in each case became slightly cloudy. The experiments were repeated except that the reaction product was filtered into mercuric chloride instead of distilled water. The same results were obtained, showing that the cloudiness was due to very fine particles of carbon which passed through the filter.

It was the object of the first experimsnts to determine the effect of heating for two minutes in the presence of a one-quarter inch brad in a volume of 5 cc. containing 2 cc. (1—1) HCl.

The results of sixteen experiments with diminishing amounts of tin under these conditions showed that with 1 mgrm. of tin the results were inconsistent, the final results of three tests being a fair cloud in the first case, a faint cloud in the second case, and a practically negative result in the third. In two tests where 2 mgrms. of tin were used, the results were also discordant. Prolonging the time of heating as well as increasing the concentration of the acid did not give uniform results. It was, however, observed that in every series of experiments the reducing action in the water-bath was not uniform. As the conditions in each set of experiments were kept constant, it appeared that the irregular results obtained were due to a lack of uniformity in the nails employed. To test this point, four blank tests were run under the conditions mentioned for the first tests, with one and one-quarter inch brads selected at random. The action in the water-bath was decidedly not uniform. At the conclusion of three minutes the acid was poured off. The nails were then washed, treated with fresh acid, and again subjected to the same tests. This was done to see whether the first treatment had eliminated any differences which might be due to variations in the surfaces of the brads. The action of the acid during the second treatment was also not uniform. Finally, the brads were examined, and it was found that the acid had so energetically attacked one of them that it was about one-half the diameter of any of the others. These results verified the conjecture that the inconsistencies in the previous tests were due to the variations in the iron nails which caused the stannic chloride to be reduced at different rates in the water-bath.

The brads employed in these preliminary tests were therefore rejected, and the previous experiment was repeated with one and one-half inch wire nails. The results were also found to be very irregular. Accordingly, one and one-half inch cut nails, or four-penny nails, were used. These gave uniform results, and were employed in all further experiments, unless otherwise specified. The

results of all further tests were classified as good or negative; good when they could readily be distinguished from the blanks run at the same time, negative in all other cases.

Having found nails to act with a fair degree of uniformity, it was the purpose of the next series of experiments to determine the separate and combined effects of the various factors which influenced the delicacy of the test. These are, first, the acid concentration; second, the time of heating; and, third, the number of nails employed. As a result of a large number of experiments, the conditions which were most favourable for the test were found; these, together with the results obtained in the final tests, are given in Table I. Under the conditions stated the results show that the smallest quantity of tin which may be detected is 0·2 mgrm. in a volume of 5 cc. The blanks obtained were practically perfect, and the results of the limit tests were very striking when compared with the blanks run at the same time. Under no circumstances could the results be mistaken.

To determine whether two nails would not give better results under the conditions of the tests in Table I., another series of experiments was performed as given in Table II. The blanks in these tests were not so good as those obtained under the conditions as in Table I, The results therefore were not so striking and conclusive. The conditions for the test as given in Table I. are therefore to be preferred.

As increasing the number of nails did not improve the test, it was thought worth while to see if prolonging the time of heating to five minutes would not give better results. To this end the experiments given in Table III. were made. The results show that extending the time to five minutes does not increase the sensitivity of the test.

Before concluding this work it was thought desirable to carry out one more set of experiments in which the conditions given in Table I. were varied both as to the time of heating as well as to the number of nails employed. The results are embodied in Table IV. The results show that the sensitivity of the test under these conditions is greater than that given in Table III.; the limiting test is, however, the same as that given in Table I. There is, however, an important difference in the quality of the blanks obtained under these different sets of conditions, and correspondingly in the decisiveness of the results. The blanks obtained under the conditions of Table I. are clearer, and as a consequence the limit tests are more readily distinguished than those of Table IV. The conditions given in Table I. are therefore to be recommended.

Influence of Antimony on the Test.—Having determined the best conditions for the iron-nail reduction test for tin when this metal alone is present, it was desirable to ascertain whether these conditions would hold good in the presence of antimony, for in most schemes of analysis the test for tin is made in the presence of antimony. Since the maximum amount of this metal in any given solution seldom exceeds 500 mgrms., and since it is customary to divide the solution containing antimony and tin into two equal portions before testing for each of these metals, 250 mgrms. of antimony (Note 4) were employed in each of the tests given in Table V. The conditions are the same as those which are afforded the maximum delicacy of the test when tin alone was present (see Table I.).

To control the results of Table V., two sets of blanks were run; one of the usual kind containing neither antimony nor tin, and the other containing only antimony. The latter were perfectly clear, and thus facilitated the detection of small quantities of tin; the former were practically clear, and could readily be distinguished when compared with the tubes containing tin. Comparison of the tubes is best made by holding them at arm's length against a dark field, such as the floor. The difference can then be very readily seen.

All the blanks which might contain any unreduced antimony were largely diluted, No precipitate formed, indicating that even after reduction there was enough free acid present to keep the antimony in solution, thus obviating the danger of mistaking a precipitate of antimony oxychloride for the test for tin.

Table I.

(Time of heating, three minutes. Acidity, 2·5 cc. concentrated HCl. Volume, 5 cc. One 1½ in. cut nail).

No.	Sn (mgrms.).	Result.
1—13	20·0—1·0	Good
14—18	0·5—0·3	Good
19—26	0·2	Good
27—29	0·1	Negative

Table II.

(Conditions same as those of Table I., except that two 1½ in. cut nails were used instead of one).

1—12	3·0—0·3	Good
13—14	0·1	Negative

Table III.

(Conditions same as in Table I., except that the time of heating was increased to five minutes).

1—14	3·0—0·3	Good
15—18	0·2—0·1	Negative

Table IV.

(Time of heating, five minutes. Acidity, 2·5 cc. concentrated HCl. Volume, 5 cc. Two 1½ in. nails).

1—13	0·1—0·2	Good
14—18	0·1	Negative

Table V.

(Time of heating, three minutes. Acidity, 2·5 cc. HCl (Note 5). Volume, 5 cc. One 1½ in. cut nail).

No	Sn (mgrm.).	Sb (mgrms.).	Result.
1—8	20·0—0·3	250	Good
9—12	0·2	250	Good

Summary and Conclusions.

1. That certain nails are unsuitable because of the irregularity of their action.

2. That in a total volume of 5 cc. with one 1½ inch cut nail the best conditions are:—Time of heating, three minutes in boiling water-bath; acidity, 2·5 cc. concentrated HCl.

3. That under these conditions the smallest amount of tin that can be detected either alone or in the presence of 250 mgrms. of antimony is 0·2 mgrm. in a volume of 5 cc.

4. That it is imperative to run a blank when the quantity of tin present is small.

II. Instead of reducing the tin with an iron nail, some analysts prefer to reduce the tin to the metallic state by means of zinc in an acid solution, and then test the solution of the precipitated tin in hydrochloric acid with mercuric chloride. This test has recently been investigated by Noyes and Bray (*Journ. Am. Chem. Soc.*, xxix., 181), who found that it possesses a delicacy of 0·5 mgrm. Our experiments confirmed their work.

III. *The Test Based upon the Reduction of Ammonium Molybdate.*—This test was first proposed by Longstaff (Chemical News, lxxx., 282), who states that it is delicate to 1 part in 1,500,000 when directly applied to a freshly prepared stannous solution. In the application of this test to qualitative analysis Baskerville finds that it is easily sensitive to 1 part of tin in 5000 (*Journ. Elisha Mitchell Scientific Society*, Feb., 1900, xvi., Part II.). As diligent search of the literature failed to disclose a record of systematic experiments performed to establish the conditions which would afford the greatest delicacy to the test when applied to stannic solutions as the starting point, the following work was uudertaken. In our work, stannic solutions were exclusively employed, for the reason that it is in this form that tin is encountered in the course of systematic analysis.

TABLE VI.

(Total quantity of acid, 4 cc. Two cc. added each time).

No.	Sn (mgrm).	Result.
1	1·0	Fair blue
2	0·2	Faint blue
3—4	0·1 - 0·05	Negative

TABLE VII.

(Total quantity of acid, 3 cc. Two cc. added first time. One cc. added second time).

1	0·1	Faint blue
2—4	0·05—0·03	Very faint blue
5—6	0·02—0·01	Negative

TABLE VIII.

(Total quantity of acid, 2·5 cc. 1½ cc. added first time. One cc. added second time).

1—2	0·1 —0·05	Faint blue
3—6	0·04—0·01	Very faint blue

TABLE IX.

(Same conditions as in Table VIII.).

No.	Sn (mgrm.).	Sb (mgrms).	Result.
1—4	1·0 —0·4	250	Good blue
5—6	0·3 —0·2	250	Fair blue
7—10	0·1 — 0 08	250	Faint blue
11—12	0·05	250	Very faint blue
13—16	0·04—0·02	250	Negative

TABLE X.

(Quantity of Sn, 1 mgrm.).

No.	Final acidity (cc.).	Result.
1	2·5	Dark blue
2	3·0	Lighter blue
3	3·5	Still lighter blue
4	4·0	Fair blue
5	4·5	Faint blue
6	5·0	Colourless or negative

The method of reducing the tin with an iron nail in acid solution was found inapplicable, because of the reducing action of the ferrous salt, formed in the reaction, upon the ammonium molybdate. Accordingly, reduction by means of zinc was tried.

After a number of preliminary experiments the following procedure was finally adopted: – To definite amounts of concentrated hydrochloric acid run into test-tubes from a burette, varying quantities of standard stannic chloride solution were added, and the volume was then made up to 5 cc. After the addition of a scant one-half grm. of chemically pure granular zinc (Note 6), the tubes were put into the boiling water-bath, and allowed to remain therein until the action practically ceased; another definite quantity of concentrated hydrochloric acid was then added (Note 7). As soon as the second reaction was completed (Note 8), the solution was diluted to 10 cc., and immediately filtered into 1 cc. of saturated ammonium molybdate solution. The results were immediately compared with a blank run simultaneously.

In the above series of experiments the total quantity of acid used in the test was gradually reduced in order that the best conditions of acidity might be found. The results are given in Tables VI., VII., and VIII.

A comparison of the results of these tables shows tha the conditions given in Table VIII. are the best, since the test becomes delicate to one part in a million. The blanks obtained throughout the work were found to possess a slight greenish blue colour which could readily be distinguished from the pure faint blue of the limit test.

Influence of Antimony upon the Test.—Having determined the most favourable conditions for the test when tin alone is present, the next step was to ascertain the influence of the presence of antimony on the test under these conditions. For reasons given earlier in this paper, 250 mgrms. of antimony were used. The results are given in Table IX. These results show that the sensitivity of the test is lowered by the presence of large quantities of antimony, and that under these conditions the limit is 0·05 mgrm. Sn.

Having found the test to work satisfactorily in the presence of the maximum amount of antimony, it was thought desirable to ascertain the influence of small quantities of this metal. The results of these tests showed that under the conditions given in Table VIII., 0·03 mgrm. of tin could be detected in the presence of 10 mgrms. of antimony, and that quautities of antimony up to 5 mgrms. are without influence on the test.

Longstaff states that an excess of acid vitiates the test by discharging the blue colour, but supplies no experimental data on this point. As some preliminary work on our part had shown this statement to be true, it was thought worth while to run a series of experiments with the object of establishing definitely the influence of acidity on the test. In these experiments the regular procedure already given was followed, except that the quantity of acid added was varied in order to yield different acid concentrations after dilution to 10 cc. The results obtained are given in Table X.

These results definitely show the influence of acidity on the delicacy of the test, and demonstrate the necessity for keeping the acidity within 4·5 cc. if a trustworthy test for 1 mgrm. of tin is desired.

Summary and Conclusions.

The investigation of the conditions under which the ammonium molybdate test for stannous tin might be applicable to stannic solutions after reduction by zinc showed: —

1. That with a total acidity of 2·5 cc. of concentrated hydrochloric acid in a volume of 10 cc., the acid being added as directed, the test is delicate to 0·01 mgrm. Sn in the absence of antimony.

2. That in the presence of 250 mgrms. of antimony the test can be used to detect 0·05 mgrm. of tin.

3. That the presence of 5 mgrms. of antimony is without influence on the delicacy of the test.

Notes.

1. Upon dilution to 1—1 the amount of free acid becomes 0·0031 grm. per cc., which in consideration of the final acidity of the solutions employed in the tests, may be neglected without any appreciable error, particularly so since the volume of the standard tin solution used never exceeded 1 cc.

2. As the volume of this tin solution employed in any test never exceeded 0·5 cc., the quantity of additional acid was 0·05 cc. This amount when compared with the quantity added in any test is so small as to be neglected without any apparent difference in the result.

3. The water-bath employed throughout this work consisted of a 500 cc. beaker half filled with water, and covered with a lead plate having six perforations large enough to accommodate the ordinary size of test-tubes. The water was heated to boiling in each case before inserting the tubes, and the boiling thereafter continued for the full time that the tubes were in the bath. This form of water-bath was found very convenient in this work, since it enabled us to perform six tests at one time. The glass beaker was preferred to the usual copper-bath, for the reason that the former permitted us to observe the progress of the reaction.

4. The solution used was made by dissolving 18·8 grms. $SbCl_3$ in HCl (1—1), and making the volume up to 100 cc.

in a volumetric flask by the addition of more HCl (1—1). The strength of this solution was 100 mgrms. Sb in 1 cc.

5. The 1·25 cc. concentrated HCl contributed by the antimony solution is included in this total of 2·5 cc.

6. A very granular form of zinc reduced the time of the reaction by reason of its readiness to dissolve in the acid.

7. In the above procedure the acid was added in two portions, the first to aid in the reduction of the tin by the zinc, and the second to re-dissolve the spongy tin which separated out. This method gave a rapid solution of the tin. If instead of adding the acid in two portions as just described, the total quantity was added at the outset, it was found that the tin did not readily go into solution on further heating.

8. In a few of the many experiments tried, an intense blue coloration was obtained, which was out of proportion to the small quantity of tin present. These results were due to the presence of minute particles of metal which passed through the filter. Hence care must be exercised in filtering.—*Journal of the American Chemical Society*, xxxv., No. 4.

THE PHYSIOLOGICAL PRINCIPLES OF HEATING AND VENTILATING.*

By Professor LEONARD HILL, M.D., F.R.S.

Lecture II.—Radiant *v.* Convected Heat.

The lecturer began by again insisting on the enormous importance of certain kinds of dust in the atmosphere. Workers in limestones have little more phthisis and respiratory disease than the general run of males, while those who work in sandstones and any process which generates silica dust, suffer very greatly and have a shorter prospect of life. The disease and the increased mortality which arises from lead and silica dust can easily be prevented, and must be prevented. He then went on to detail the experiments which prove that there is no organic poison in exhaled air, and that the increased percentage of carbonic acid and diminished percentage of oxygen in the air of crowded rooms had nothing to do with the symptoms of discomfort felt therein.

Prof. Hill then dealt with the physical conditions of the atmosphere, the heat, moisture, and movement, which he said profoundly affected the health and vigour of the body. Wrong physical, not chemical, conditions of the atmosphere cause all the discomfort of crowded rooms.

Body heat (its production and its diminution) was discussed, and the effects of body heat stagnation described. It was pointed out how a warm still atmosphere depresses the activity of the body, the oxygen intake, and the vigour of the circulation, together with the appetite for and digestion of food.

The importance of cutaneous sensations and the depressing effect of monotony of atmospheric conditions were brought into prominence. A new instrument for measuring the rate of cooling, the Kata-thermometer, was described, and the failure of the ordinary thermometer to indicate the proper conditions for body comfort and health illustrated. Observations taken with the Kata-thermometer in and out of doors at the seaside were mentioned. The natural conditions on ideal summer days were described, and the advantages of radiant heat and cooling moving air insisted on. The wastefulness and the pollution of the atmosphere by the open fires impelled us towards the use of the modern gas fire, which gave 50 per cent of the energy of the fuel as radiant heat. Artificial heat, and particu larly air heated by convection, was not good for us, and ought always to be associated with open windows.

* Chadwick Public Lectur s, Bristol, 1913. (Delivered at Bristol University, October 30. The Lord Bishop of Bristol in the Chair)

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Seven Grms. of Radium in the Whole World!

A quite recent census concerning the quantities of salts of radium existing at the present time in the different scientific and medical laboratories of the globe, shows us that there are not more than six or seven grms. of metallic radium in the whole world. The industry of radium was born in 1899 from the impulse given to it by the studies of Pierre Curie. At a lecture given at the Society of Civil Engineers, M. Paul Besson has just now recalled the fact, that from that period till 1904, from 13 tons of pitchblende residuum, it was only possible to extract about 2 or 3 grms. of radium, which served specially to supply the laboratory of M. and Mdme. Curie. But an Austrian law put a stop to the exportation of the radio-active ores of Joachimstal. Radium was then extracted in France from much poorer ores containing only from a half to two mgrms. of radium per ton, such as the antimonites which come from Portugal or the carnotites from Colorado, whereas the residues of pitchblende contained from 100 to 200 mgrms. of radium per ton. During the last few years Austria has not treated more than 3 or 4 tons of pitch-blende per year, from which were extracted annually less than 1 grm. of radium. America and England do not as yet produce radium salts. It is France which at present controls the production and the market of the precious metal. The price of a grm. of hydrated bromide of radium remains about 400,000 francs (£16,000) more or less, which means that a grm. of pure metallic radium is worth about 780,000 francs (£31,200). The principal possessors of radium are Mdme. Curie, whose laboratory contains from about 2·6 grms. to 3 grms. of radium, and Sir Ernest Cassel of London. As to the different applications of radium, they are well known. Besides its employment in medicine and therapeutics, its use in industry is spreading more and more. It has been possible to realise, with this metal, certain apparatus enabling the measurement of the potential of a conductor at a distance, without contact. Lastly, in silk factories, radium has been employed for de-electrifying not only the textile fibres but also parts of the machinery.

Gallium is Not Rare.

After a long series of researches, guided by the works or Mendeleeff, one of the rarest of metals, "gallium," in the blende of Pierrefitte, by the French chemist Lecoq de Boisbaudran, in 1875, has just been found in commercial aluminium. M. J. Bardel, director of one of the services of the Institute of Hydrology of the Collège de France, and M. C. Boulanger have made a spectrographic examination of ordinary aluminium, and in it they discovered the presence of "gallium." In a paper presented by Professor Haller, in their name, the two chemists indicate that, in treating 2 kilogrms. of aluminium, they have obtained nearly 4 decigrms. of gallium. Ordinary aluminium contains, then, nearly 0·02 per cent of this metal supposed to be so rare. It is a greater percentage than that attributed by Lecoq de Boisbandran to the blende of Pierrefitte.

Signs of Fatigue.

After having studied the conditions of very hard work with the physiological limits of fatigue, M. Jules Amar, in a new paper presented before the Academy of Sciences by Professor Dastre, has just examined what are the respiratory signs of fatigue. A double pneumograph, held in place during the whole duration of the experiment, has tracings of respiration that were easily compared. On the other hand, the gaseous outputs of the respiration were measured every two minutes. The alimentation of the persons under survey was the same for all: a simple cup of coffee well sugared, two hours before taking measurements. These conditions being established, M. Jules

Amar remarked that the frequency of the respiration increases with the work, but without any rigorous proportionality. It is, on an average, thirty-two respirations per minute, for the usual speed of a workman. With great speed fatigue is produced and puts an end to the work when it is hardly begun; that is to say, at the end of four minutes at the most. The frequency of the respiration is then somewhere about forty. Amplitude also increases with the work. The respirations are deeper and still deeper; they are barely more than twice as deep as when at rest. But if the work is continued till fatigue ensues, the amplitude of the respirations diminishes gradually and different irregularities are to be remarked. If the work is very hard, by an excess of effort or speed the respiratory output is irregular with accentuated ups and downs, but as a rule it goes on increasing until loss of breath occurs.

Election of Non-Resident of the Academy of Sciences—J. H. Fabre's Candidateship Withdrawn.

The fourth chair for a non-resident member of the Academy of Sciences—a section newly created by the decree of the 17th March, 1913, and reserved for provincial scholars—has been awarded to M. Charles Deperet, Dean of the Faculty of Science of Lyons, and to whom are due numerous and interesting geological works. His researches embrace the tertiary history of the Mediterranean basin. M. Deperet was elected with thirty-two votes, and the entomologist, J. H. Fabre, obtained two votes. We believe that at the secret committee meeting, held after the public sitting, the two eminent naturalists who had voted for the entomologist of Serignan, whose whole life has been consecrated to the study of the habit and lives of insects, have withdrawn his candidateship. In a written notice they said they said that J. H. Fabre had not stood for election, considering, on the other hand, from the votes of the commissions already elected, that he was not likely to succeed; the two savants not wishing to expose a man of M. Fabre's age to the humiliation of being refused, they simply withdrew his candidateship, which they themselves had proposed.

The High Atmosphere.

The results of the Franco-Swedish exploration of the high atmosphere during the three campaigns from 1907 to 1909, undertaken by Professor Hildebrandsson, of Upsala, and the late regretted Tesserenc du Bort, have just been published by M. Meurice, who took part in the expedition. M. Deslandres, Director of the Observatory of Meudon, recalls to mind that it is to Tesserenc du Bort that is due the discovery of the stratosphere, a layer of isothermal air whose temperature, extremely low, is constant through a great thickness. This layer, discovered for the first time at the Observatory of Trappes, at an altitude of from eight to ten kilometres, has again been found at the Equator at a still higher altitude, and its temperature there is somewhat lower. In the polar region, at Kiruna, situated at the north of the Scandinavian peninsula, Hildebrandsson and Tesserenc du Bort remarked the presence of the same isothermal layer. Numerous soundings with pilot balloons have allowed it to be proved that the temperature of the stratosphere was the same as that observed at Trappes. However, there is a difference between the temperatures of the lower layers of Lapland and of France. Nearly all the pilot balloons sent up by the two meteorologists have been recovered. M. Delandres has also announced that the Minister of War was about to accept the observatory of Trappes, which is offered to him by the Tesserenc du Bort family.

Physical Society's Annual Exhibition.—This Exhibition will be held on Tuesday, December 16th, at the Imperial College of Science, and will be open both in the afternoon and evening.

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF CHEMISTRY.

At a Meeting of the Institute of Chemistry held at the Imperial College of Science and Technology, South Kensington, on Wednesday, October 29th, Prof. R. Meldola, LL.D., F.R.S., in the Chair, the first of two lectures was delivered by W. P. Dreaper, F.I.C., on "*The Research Chemist in the Works, with special reference to the Textile Industry*."

The lecturer pointed out the difficulty in expressing opinions which could be universally accepted, for industrial chemists worked under such varying conditions and were influenced by temperament and past training. His remarks should therefore be taken as applying especially to the textile industry.

The total gross value of the Textile Industry (First Census of Production, 1907) indicated that the value of the textile materials and fabrics manufactured in the United Kingdom amounted to the total of £333,000,000; and that 1,253,000 persons were employed in their manipulation. Power to the amount of 1,900,000 h.p. was utilised, and 77 per cent of the firms used coal to the value of £8,137,000. On a basis of one chemist for every 2000 persons employed, no less than 600 chemists would be utilised in this industry alone; each of whom would deal with an annual gross output valued at over £500,000. A saving of 10 per cent in the coal bill would amount in all to £1,000,000. It would be remembered that one large aniline dye combine on the Continent already employed no less than 700 chemists. The recently made statement that "Science was fast becoming an industry" seemed to apply in this case at any rate.

Stress was laid upon the value of a satisfactory knowledge of the principles underlying analysis to the student entering a works. He must expect to work on the borderland of industrial research, and therefore to devise new methods of a chemical or physical nature to record his progress. Actual examples were given of the difficulties met with in interpreting the figures obtained. The results that the successful investigator might achieve by working out new methods and processes, or improving those already employed in works, were indicated, and the advantages of secret working were also dealt with. Also the effect produced through the stress of competition and the utilisation of new processes on working conditions. It was urged that the chemist should spend as much of his time as possible in the works, entering the laboratory when systematic investigation was necessary. The industrial chemist who remained in his laboratory was lost. Knowledge of chemistry alone was an insufficient equipment, modern research being set on a wide basis, and requiring a knowledge of physics and the power to apply this in many directions. This was demonstrated at every turn.

After describing a typical college dyeing department, the fitting up of a works research laboratory was briefly considered. It was pointed out that experiments utilising more than 5 to 10 h.p. should be conducted in the works itself. The fitting up of experimental works as a preliminary to establishing an industry was discussed. Such a station had been known to utilise 10,000 h.p. for experimental purposes.

The work of the textile chemist was then considered in greater detail, and specially illustrated by reference to the early developments in Mercerising and Schreinering. Both these processes were shown to depend upon certain details, which although actually patented in the former case were not fully realised in the early experiments. The chemist working under industrial conditions would at once realise the success achieved by the rule-of-thumb man in the past; by systematically studying his methods, and seeking to discover points he had not fully realised, the chemist may often be able to improve upon them. Workmen who control operations of vital importance should be "discovered"

by the chemist; their methods studied in the light of his more specialised knowledge. Important results could often be secured by inquiring into the origin of so-called defects in manufacture.

The nature of the methods and machinery used for producing artificial fibres, and more recently artificial fabrics, was then indicated; samples being exhibited of many of the different products already obtained. The part to be played by the chemist was pointed out, as well as the great need for further research in this direction.

The remaining portion of the lecture dealt with the influence of theory and the chemist's work on actual industrial operations, and concluded with a brief discussion on the modern theories in connection with dyeing and investigations which have had their origin in observations originally made in the dye-house.

NOTICES OF BOOKS.

The Volatile Oils. By E. GILDEMEISTER and Fr. HOFFMANN. Second Edition by E. GILDEMEISTER. Translated by EDWARD KREMERS. Volume I. London, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE second German edition of this treatise has been expanded into two volumes, the first of which deals with the history of the several volatile oils, and also contains descriptions of the chief constituents of the oils and of methods of examining and testing them and detecting adulterants. The history of methods of distillation from those employed in primitive times down to the most modern processes is fully treated, this part of the book having been written by the late Dr. Friedrich Hoffmann, and only very slightly altered in the new edition. A new chapter has been added on the production of flower perfumes by extraction, enfleurage, and maceration, while the chapter on the theory of the separation of the ethereal oils by distillation has been omitted. The translator has thought it advisable to condense some chapters to a certain extent, but, on the other hand, he has added details of a few oils to the special part, and has included some new results which have been published quite recently.

Production et Consommation des Engrais Chimiques dans le Monde. ("The World's Production and Consumption of Chemical Manures.") Rome: Institut International d'Agriculture. 1913. (3 francs.)

THIS monograph has been prepared for the Committee of the Italian Bureau of Agricultural Intelligence and Plant Diseases, by Dr. G. A. R. Borghesani, who has taken the utmost trouble to collect all the latest reliable data and arrange them in the most accessible and convenient form. He addressed a circular letter to the Governments of practically all the countries of the world asking for information as to the production and consumption of manures, and from their replies, which were in most cases very detailed, he compiled the statistical tables which occupy a large part of the monograph. He also visited many European countries for the purpose of getting a first-hand knowledge of many details. Although necessarily far from complete the monograph will provide a valuable foundation for future work on the subject; it is intended to issue half-yearly summaries of the production and consumption of fertilisers, and thus keep the information quite up to date.

Canadium, the Supposed New Element.—In the Annual Report of the British Columbia Minister of Mines it is stated that authentic samples of the dyke in which the presence of platinum metals and "canadium" had been reported, were procured and submitted, together with concentrates from the crushed material, to representative firms of assayers, to the Canadian Geological Survey, and to the British Columbia Government Laboratory. In no case were any traces of platinum metals detected, nor was there any evidence of the presence of the alleged new metal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 9, September 1, 1913.

This number contains no chemical matter.

Vol. clvii., No. 10, September 8, 1913.

Experiments on the Cupric Hydrates and the Heat of Formation of Copper Nitrate.—M. de Forcrand.—Péligot's hydrate of cupric oxide, $CuO.H_2O$, does not lose weight even when kept over sulphuric or phosphoric acid at 30°. When heated to 85° it changes colour, becoming green, but does not lose weight. If heating is continued it begins to undergo hydration; thus at 100° it becomes olive green, and its formula corresponds to $CuO + 0{\cdot}8H_2O$. It then turns brown, and is converted into the hydrate $CuO + 0{\cdot}35H_2O$. By determining the heat of solution of these different hydrates in dilute nitric acid it is found that the isomeric change of the blue into the green hydrate is exothermic and corresponds to 0·261 cal. The heat of formation of anhydrous copper nitrate is 71·49 cal., and for a solution 81·96 cal. These values approximate closely to those obtained for uranyl nitrate, and the mean for the two metals is the same.

Mechanism of the Formation of Sulphuric Acid in the Lead Chambers.—E. Briner and A. Kuhne.—When sulphuric acid is produced in the lead chambers the atomic oxygen set free by the dissociation of NO_2 into NO and O plays an important part; the atoms of oxygen combine with SO_2 far more readily than molecules, and they are continually regenerated by the dissociation of NO_2. The anhydride SO_3 readily gives H_2SO_4 with water, and in consequence of its low vapour tension at the temperature of the chambers (40—60°) it rapidly condenses.

MEETINGS FOR THE WEEK.

TUESDAY, 11th.—Chadwick Public Lectures, 5. (The University of London, South Kensington). "The Place of the Open-air School in Preventive Medicine," by Sir George Newman, M.D.

WEDNESDAY, 12th.—Biochemical Society, 5.30. (In the Physiological Laboratory, King's College, London).

THURSDAY, 13th.—Royal Society. "The Preparation of Eye-preserving Glass for Spectacles," by Sir William Crookes. "On An Inversion-point for Liquid Carbon Dioxide in regard to the Joule-Thomson Effect," by A. W. Porter. "Negative After-images and successive Contrast with Pure Spectral Colours," by A. W. Porter and F. W. Edridge-Green. "The Positive Ions from Hot Metals," by O. W. Richardson. "Diurnal Variation of Terrestrial Magnetism" and "A Suggestion as to the Origin of Black Body Radiation," by G. W. Walker.

FRIDAY, 14th.—Physical, 8. "Thermal Conductivity of Mercury by the Impressed Velocity Method," by H. R. Nettleton. "Polarisation and Energy Losses in Dielectrics," by A. W. Ashton. A Lecture Experiment to illustrate Ionisation by Collision and to show Thermo-luminescence, by F. J. Harlow.

—— Alchemical Society, 8.15. (At International Club, Regent Street). "The Hermetic Mystery," by Mdme. Isabelle de Steiger.

The Proprietor of PATENT No. 22506 of 1910, for "Improvements in the Manufacture of Pure Tetra-Phosphortrisulphids," is desirous of disposing of the Patent Rights or of negotiating for the grant of Licences to work thereunder.

All enquiries should be addressed to JOHNSONS and WILLCOX, 47, Lincoln's Inn Fields, London, W.C.

The Owners of BRITISH PATENT No. 29886 of 1909, entitled "Improvements in Processes of Extracting Turpentine, Oils, and other Products from Wood," are desirous of disposing of the Patent or entering into working arrangements, under Licence or otherwise, with firms likely to be interested in the same.

A copy of the Patent Specification and full particulars can be obtained from and offers made (for transmission to the owners) to MARKS and CLERK, 57 and 58, Lincoln's Inn Fields, London, W.C.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2816.

THE CONSTITUTION AND STRUCTURE OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS.

THERE are two methods employed by scientists of discovering scientific truths :—

(*a*) Discovery by direct experiment ; *e.g.*, the fact that radium splits up into helium and niton.

(*b*) Discovery by reasoning upon several allied experimental facts ; *e.g.*, the discovery of Newton's First Law of Motion.

The former method, which of course must precede the latter, only discovers isolated truths, and does so in new directions generally by accident ; *e.g.*, the discovery of the fact that helium and oxygen can combine to form neon was accidental. The latter method, if correctly done, has a great advantage over the other, for it must of necessity show the way to further discoveries since it demonstrates the reason of things. The results of reasoning are sometimes for ever incapable of proof by direct experiment ; *e.g.*, Newton's First Law of Motion. Some results of reasoning may be incapable of direct experimental proof under our present knowledge, although the conditions may be altered by the advancement of knowledge. An example of this is afforded by the present condition of the facts which demonstrate the constitution and structure of atoms. The elucidation of this statement will appear in the following matter.

The following discoveries have been made in duplicate by the two methods within the last ten years :—

In an α-ray change, when a helium atom carrying two atomic charges of positive electricity is expelled, the element changes its place in the Periodic Table in the direction of diminishing mass and diminishing group number by two places.—Prof. F. Soddy, 1911.

The non-metallic nature of an element is always due to a pair or pairs of electropositive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity.—Advt. in *Nature*, June 14, 1906, asking for expert opinions.

If there is any difference between these two statements it would be interesting to know what the difference is, for the latter statement is exactly the same as the following : —"If a helium atom (at. wt. 4) carrying two charges of positive electricity could be expelled from several of the simple elements. the residual product would be two places lower in the Periodic Table, since the element would have lost two valencies together with a mass of 4."

The statement on the left was obtained by direct experiment from the *radio-active* elements ; that on the right from reasoning upon facts with regard to the *simple* elements.

An element, whose atomic weight is 3, is the only element of low atomic weight which has been discovered within the last ten years. It is found by Sir J. J. Thomson to be given off by all kinds of substances, a fact which leads him to think sometimes that the elements of low atomic weight are splitting up.

H_3 is the only new element, which was discovered ten years ago by reasoning to be a necessary part in the constitution and structure of nearly all the simple elements, and it was printed in the CHEMICAL NEWS of March 24, 1910 (vol. ci., p. ii.) as an element, and called H_3 (Asterium).

Messrs. Collie and Patterson discovered this year (1913) that helium and oxygen can combine to form neon.

In the CHEMICAL NEWS of March 24, 1910 (vol. ci., p. ii.) the structure of neon was given as the combination of the structures of helium and oxygen.

It is absolutely impossible for any one to integrate facts to such a degree of detail so as to be in accordance with the latest discoveries of modern science, and yet not to have obtained the truth.

It follows from this that the first main principle in the constitution and structure of all the chemical elements, whether radio-active or otherwise, has been *proved ;* and it is this :—"In a large number of the elements two electropositive valencies emanate from a portion of the element of which the mass is 4."

If the body of atomic weight 3 observed by Sir J. J. Thomson is not a product of the disintegration of some of the simpler elements, and if it is simply absorbed in some manner by nearly all kinds of substances, then all the *exact* determinations of the atomic weights of the elements are completely upset, and it is quite absurd for scientists to say that it has been proved, for instance, that the atomic weights of elements are not all whole numbers.

The presence of this terribly large source of error must be worrying the International Committee on Atomic Weights, since it seems to be necessary for scientists to expel all traces of it and start the determination of the atomic weights all over again.

But, since the atomic weights of several of the common and important elements, *e.g.*, B, C, F, O, and Na, are now given as exactly whole numbers, it is evident that this source of error cannot have affected them, for it is quite impossible for scientists to arrive at these beautiful results and yet not to have obtained the truth. Therefore, Sir J. J. Thomson's X_3 is not an impurity, but is a product of the disintegration of the simpler elements.

Prof. F. Soddy said in the CHEMICAL NEWS in the early part of this year (cvii., 97), that all attempts to find numerical relations between the atomic weights of the elements had ended in failure. It is evident, therefore, that the most obvious relationship which was ever discovered has been stowed away, forgotten, and ignored by scientists. It was published by the CHEMICAL NEWS, in a paper, not as an advertisement. (Results put in as advertisements by the author are those which are likely to be outrageous to scientists of the time).

The discovery was as follows :—"Considering only elements of atomic weight less than 60 (because the possible errors in numerical data for elements of low atomic weight are less than for those of high atomic weight), *whenever the atomic weight of an element approximates to, or is nearer to, an even whole number, its valency is even, and when it approximates to, or is nearer to, an odd whole number, its valency is odd*, with the possible exception of nitrogen.

This fact, taken in conjunction with the fact that an error in the determination of atomic weights must have arisen from the observance that protyle, which is something like the thousandth or two-thousandth part of the mass of an atom of hydrogen, can be expelled from nearly all substances, and also taking into consideration the fact that the atomic weights of the elements are evidently hovering round whole numbers, *proves that the atomic weights of the elements are whole numbers.* For, if not, what do they mean by hovering round whole numbers, and why are 7 out of 28 given as exactly whole numbers, and why are 21 out of 28 not more than 0·1 from whole numbers ?

The facts with regard to this matter are now placed in tabular form. (See accompanying Table).

In *Nature*, December 26, 1901, it is asserted that glucinum is probably a triad, but the Periodic Law stands in the way. The "Periodic Law" has no business to stand in the way, for it is not a law, but only an ex-

Element.	Atomic weight (1913).	Difference from whole numbers.	N earest whole number.	Remark.	Maximum valencies.	Remark.
Hydrogen	1·008	0·008	1	Odd	1	Odd
Helium	3·99	0·01	4	Even	2	Even
Lithium	6 94	0·06	7	Odd	1	Odd
Glucinum	9·1	0·1	9	Odd	3	Odd
Boron	11·0	0·0	11	Odd	3	Odd
Carbon	12·0	0·0	12	Even	4	Even
Nitrogen	14·01	0·01	14	Even	6 (?) (NO_3)	Even
Oxygen	16·0	0·0	16	Even	2	Even
Fluorine	19·0	0·0	19	Odd	1	Odd
Neon	20·2	0·2	20	Even	0	Even
Sodium	23·0	0·0	23	Odd	1	Odd
Magnesium	24·32	0·32	24	Even	2	Even
Aluminium	27·1	0·1	27	Odd	3	Odd
Silicon	28·3	0·3	28	Even	4	Even
Phosphorus	31·04	0·04	31	Odd	5	Odd
Sulphur	32·07	0·07	32	Even	6	Even
Chlorine	35·46	0·46	35	Odd	7	Odd
Potassium	39·10	0·1	39	Odd	1	Odd
Calcium	40 07	0·07	40	Even	2	Even
Argon	39 88	0·12	40	Even	0	Even
Scandium	44·1	0·1	44	Even	4 (ScO_2)	Even
Titanium	48·1	0·1	48	Even	4	Even
Vanadium	51·0	0·0	51	Odd	5	Odd
Chromium	52·0	0·0	52	Even	6	Even
Manganese	54·93	0·07	55	Odd	7	Odd
Iron	55·84	0·16	56	Even	4 or 6 (ferrates)	Even
Cobalt	58·97	0·03	59	Odd	3	Odd
Nickel	58 68	0·32	59	Odd	3 (Ni_2O_3)	Odd

ceedingly useful observation. Who ever heard of a law which makes an indefinite statement? It asserts that "the properties of elements are periodic functions of their atomic weights." What functions? Nobody has yet been able to discover. It follows from this law that specific gravity (*e.g.*) is *a* periodic function of atomic weight. The word "a" here is the *indefinite* article, and has no business to appear in the statement of a *law*. It denotes uncertainty. In Newton's First Law of Motion the word "a" occurs, but there is no uncertainty in it. The law is as follows:—Every body remains in its state of rest or of uniform motion in *a* straight line, unless it is compelled by some external force to alter that state.

The remark, which is continually occurring in scientific papers, that the Periodic Law requires amendment, is evidently fully justified.

The Periodic observation is now out of date, for it was merely an observation, the reason for it being then unknown; but the reason is now known, and therefore must take the place of the observation.

The mathematical probability that the two columns of remarks on even and odd whole numbers would exactly correspond *by accident* is $1 : 2^{28}$, *i.e.*, 1 : 268,435,456.

The probability that they would accidentally correspond with only one exception is $1 : 2^{26}$, *i.e.*, 1 : 67,108,864; with only two exceptions, $1 : 2^{24}$, *i.e.*, 1 : 16,777,216; with three exceptions, 1 : 4,194,304; with four exceptions, 1 : 1,048,576.

If any one thinks that there are as many as four exceptions, even then it has been proved that the probability is at least one million to one that the correspondence is not the result of an accident, and the general rule holds that if the atomic weight of an element approximates to an even whole number its maximum valency is even, and if the atomic weight approximates to an odd whole number, its maximum valency is odd.

This general rule, taken in conjunction with all available facts, leads to the deduction published (as stated) in *Nature* on June 14, 1906.

Supposing that it is admitted that nitrogen is certainly an exception to the general rule, although the molecule NO_3 has been recorded, many scientists would say that this exception upsets the rule; but it does not do anything of the kind—it proves the rule.

If any one thinks that an exception does not prove the rule, he is asked to consider the following statement:—"The solar system is composed of an approximately spherical body, called the Sun, round which revolve approximately spherical bodies, called Planets, around which revolve approximately spherical bodies, called Satellites." This is the general rule. But the fact that Saturn is accompanied by rings as well as satellites, does not upset the general rule. It only emphasises it, and leads to something deeper; for the rings of Saturn may be in the process of disclosing to us the method by which satellites are produced.

If, after what has been said, scientists are prepared to consider the second main principle in the constitution and structure of atoms, which is a more general observation than the first, it is ready to be produced; but, if not, it will have to wait for a more convenient season. It would not do scientists much harm to condescend to look at it. It might do a little good in showing the way to further successful experiments.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

(Continued from p. 229).

Group III.—There have been many attempts to isolate hydrogen boride, which is formed when magnesium boride is acted on by acids and which colours the flame of the simultaneously evolved hydrogen green, and which is also recognisable by its bad odour. The amount of hydrogen boride present is exceedingly small and it is so unstable that until very recently all efforts to isolate it for analysis have been futile, although Ramsay and Hatfield considered it probable that the formula of the gas they obtained was H_3B_3. Stock and Massenez (*Ber.*, xlv., 3539) have now in part solved the problem and their results are a surprise, for the simplest gas evolved in the above reaction is $H_{10}B_4$, and this is accompanied by another whose formula is probably $H_{12}B_6$, as well as others, apparently formed by

* *Journal of the American Chemical Society*, xxxv., No. 2.

the decomposition of the latter, which were present in too small quantity to be studied. The difficulties of previous experimenters has arisen from the small quantities of the borides formed, their great instability, especially in the presence of water, the difficulty of separating the different borides formed in the reaction, and the unavoidable presence of at least the hydrogen silicides, from the silicides in the magnesium boride used. The hydrogen borides were prepared by letting the finely powdered magnesium boride fall slowly into acid, and condensing by liquid air, the total yield being under most favourable circumstances 1·2 cc. per litre of evolved hydrogen. The liquid obtained was fractioned, and after great difficulties sufficient of the above compounds obtained for study. $H_{10}B_4$ boils at 16° and $H_{12}B_6$ at a higher temperature, probably near 100°. Both ignite in contact with the air, and decompose in water, giving compounds similar or identical with those described by Travers and Ray. These chemists (*Proc. Roy. Soc. London*, (A) lxxxvii., 163), by fusing a mixture of magnesium powder with B_2O_3 in hydrogen, obtained a grey powder which, when treated with water, slowly evolved a gas. The solution became yellow and was slightly alkaline. On boiling this solution hydrogen is given off and when treated with acid still more copiously. The gas has a peculiar odour and burns with a green flame, but analysis shows it to be nearly pure hydrogen. It apparently contained traces of a boron hydride (as Stock has found). On distilling the solution a compound passes over which has the formula B_2O_3, but which is not boric anhydride, though evidently an isomer of it. The authors consider that the original powder contains not only Mg_3B_2 but also Mg_2B_4; that from these are formed by the action of water B_4O_2 and B_4O_3, which are further acted on by the water with the formation of the oxide B_2O_3 above mentioned and "boron hydrates" (a name not well chosen) of the respective formulæ $B_2O_2H_6$ and $B_2O_3H_6$.

In the continuation of his work on Scandium, Meyer (*Nernst-Festschrift*, cccii.; Chem. News, cvi., 13) calls attention to the fact that unless a very large excess of KIO_3 is used in separating thorium from scandium, a small amount of thoria remains dissolved in the solution of scandium iodate. This scandium, and also scandium separated by the sodium carbonate method, showed no radioactivity and was spectroscopically pure, yet had an atomic weight of 45. Further purification with KIO_3, with great sacrifice of scandium, brought the atomic weight down to 44, and thorium could be identified in the portion precipitated. It is thus possible for scandia to contain upwards of 0·5 per cent thoria which cannot be detected directly by chemical or physical means. However, Meyer shows that the magnetic method of detection is available, since the product with atomic weight of 45 is paramagnetic, while the pure product (44) is diamagnetic. He calls attention to the fact that scandium, lanthanum, and yttrium, which unquestionably belong to the third group of the periodic system, are distinguished by their magnetic character from all the other rare earths. Among the other works which have appeared on the rare earths are those of James (*Journ. Am. Chem. Soc.*, xxxiv., 757) on their separation; of Jantsch (*Zeit. Anorg. Chem.*, lxxvi., 303) on the double nitrates; of Wirth (*Ibid.*, 174) on the solubility of the oxalates and sulphates in sulphuric acid; and of Barnebey (*Journ. Am. Chem. Soc.*, xxxiv., 1174) on the reactions of the rare earths in non-aqueous solutions. Urbain and Bourion (*Compt. Rend.*, cliii., 1155) have also prepared and studied the chlorides of europium, $EuCl_3$, $EuCl_2$, and EuOCl. These papers are all valuable contributions to this interesting subject, but do not lend themselves to brief abstraction.

Group IV.—The question as to what is the first reaction that takes place when carbon burns in oxygen has long been a subject of controversy. The commonly accepted view that the initial combustion is to CO_2, which in the presence of incandescent carbon is reduced to CO, rests experimentally chiefly on the work of Lang, who found that in a slow oxygen stream carbon was oxidised at 500° almost exclusively to CO_2, while no CO_2 was reduced to CO at this temperature. The formation of *some* CO in a more rapid gas current Lang attributed to local heating, which did not occur in the slow current. The conclusions drawn from these and other experiments by Lang were called in question by Dixon, and his experiments and those of Baker on explosion of rates seemed to show that at least in the case of gaseous carbon the formation of CO precedes that of CO_2. C. J. Baker also showed that while moist oxygen absorbed by carbon at −12° was given up as CO_2 when the carbon was heated to 100°, dry oxygen (by P_2O_5) absorbed by dry carbon at +12° was not given up till 450° and then mainly as CO, it appearing thus that CO is the first product of oxidation. Rhead and Wheeler (*Journ. Chem. Soc.*, ci., 831, 846) have approached the subject from the standpoint of determining the velocity of the reaction (*a*) $C+O_2=CO_2$; (*b*) $CO_2+C=2CO$; (*c*) $2C+O_2=2CO$; and (*d*) $2CO+O_2=2CO_2$, at different temperatures. If it could be shown that either reaction (*a*) or reaction (*c*) proceeded at a temperature at which, under the same experimental conditions, the rates of reactions (*b*) and (*d*) were inappreciable, the problem would be solved. It was, however, not found possible to obtain a temperature at which the velocity of carbon oxidation was appreciable, where there was conclusive evidence of the primary formation of either oxide to the exclusion of the other. Some CO is produced by the oxidation of carbon at low temperatures under conditions which do not admit of its being formed by the reduction of CO_2, but on the other hand CO_2 is undoubtedly produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that CO is first formed and then oxidised to CO_2. The conclusion is therefore drawn that when carbon is burned at low temperatures CO_2 and CO are produced simultaneously, a conclusion quite in accord with practically all previous experimental evidence. A further paper is promised on what reaction between carbon and oxygen can account for this simultaneous production of two oxides. The question as to whether carbon monoxide burns directly to the dioxide $2CO+O_2=2CO_2$, has in the past stimulated much investigation, especially since it seems certain that the reaction does not go on, even at high temperatures, unless at least a trace of water is present. Now Wieland (*Ber.*, xlv., 679) has shown that carbon monoxide is oxidised by moist palladium black, even in the absence of oxygen. It appears that the first step of the reaction is the union of CO and H_2O to formic acid, and that this is in turn decomposed to CO_2 and hydrogen, the latter being absorbed by the palladium black. If the same reaction goes on in the ordinary combustion of carbon monoxide, then the hydrogen evolved is at once oxidised to water and the cycle repeated. Wieland was able to show the formation of formic acid in the combustion of carbon monoxide by directing the flame against ice, when formic acid was detected in the water.

An examination of the air collected on the Charcot Antarctic expedition has been made by Müntz and Lainé (*Compt. Rend.*, cliii., 1116) and the amount of CO_2 found to vary from 1·447 to 2·553 parts per 10,000. the mean being 2·0524. The small amount compared with the normal content is to be accounted for by the temperature of the ocean water, generally below 0°, thus reducing the dissociation pressure of the dissolved bicarbonates. This is in confirmation of the theories of Schloesing, and shows that, contrary to the idea of Gay Lussac, the movement of the atmosphere is not sufficient to cause a uniform distribution of CO_2. It is to be hoped that there will soon be opportunity for a study of the atmosphere over the Antarctic plateau, where the influence of the ocean would be eliminated. The composition of the higher layers of the atmosphere is considered by Wegener (*Zeit. Anorg. Chem.*, lxxv., 107) to be very different from that of the lower strata. His views are based on the changes of density as shown by the suspension of the Krakatoa dust

clouds, diffuse reflection of light, and also of sound, the glow of meteors and spectra of the aurora and of meteor trails, and also the analogy of the sun's atmosphere. At 40 kilometres oxygen is reduced one-half and nitrogen correspondingly increased. Above this these gases rapidly decrease, while hydrogen increases and helium is at a maximum of 4 per cent. At 200 kilometres and above, the chief constituent is a gas lighter than hydrogen, called by Wegener geo-coronium, resembling the coronium of the sun, and possibly identical with Mendeleéff's element with atomic weight of 0·4.

A further substantiation of the theories of Franklin on ammono-compounds, fully recapitulated by him and also applied to the mercury ammonia compounds (*Am. Chem. Journ.*, xlvii., 285, 361), is furnished by the work of Ruff (*Ber.*, xlv., 1364) on the nitrogen compounds of quadrivalent titanium. The starting-point was $TiBr_4$, formed by the action of bromine in a stream of carbon dioxide on metallic titanium or its carbide. On treatment with ammonia this gives an ammonate of approximately the composition $TiBr_4.8NH_3$. By washing with liquid ammonia this is more or less ammonolysed, giving a product (ammono-basic bromide) containing both titanium amide, $Ti(NH_2)_4$, and bromide, of somewhat variable composition. From this, by action of potassamide, KNH_2, there was formed a new titanium nitride, Ti_3N_4, and a potassium ammono titanate of the formula $KHTiN_2$ (structurally, $\begin{matrix}KN\\HN\end{matrix}\!\!\geqq\!\!Ti$). The nitride, Ti_3N_4, is hydrolysed by water with the formation of titanic acid and ammonia, and on heating is converted into the nitride of trivalent titanium, TiN, and nitrogen. The possibility of utilising this reaction for the synthesis of ammonia from its elements is suggested by the author, and an experiment of heating a mixture of hydrogen and nitrogen to 360° in the presence of the above-mentioned potassium salt showed a contraction of volume, which indicated ammonia formation. The potassium ammono-titanate ignites spontaneously in the air and is violently decomposed by water. A portion of the potassium (3/10) can be removed by washing sufficiently with liquid ammonia. With potassium iodide or sulphide the potassium seems to be replaced by iodine or sulphur, indicating, as would be expected, the amphoteric nature of the TiN_2 group.

Group V.—A rather extensive piece of work has been carried out by Ferratini (*Gazz. Chim. Ital.*, xlii. [1], 138) on the double salts of hydrazine. These were generally prepared by mixing solutions of the components, if soluble, but occasionally by solution of the oxide or halide in an acid solution of the hydrazine salt. In many cases, especially with bivalent metals, the salts were hydrated, and in a few cases contained "hydrazine of crystallisation" (hydrazinates). No systematisation of the types appears possible. For example, Cu^{I} gives $3CuCl.N_2H_5Cl$, $CuCl.N_2H_5Cl$, $CuCl.N_2H_5Cl.0{\cdot}5H_2O$, $3CuBr.2N_2H_5Br$, $2CuCN.N_2H_5CN$; Sb and Bi give the $SbCl_3.3N_2H_5Cl$ type, but Fe$''$ and Mn$''$ give the same, as $FeCl_2.3N_2H_5Cl$; while Co and Ni give $CoCl_2.2N_2H_5Cl.2{\cdot}5H_2O$ and $CoCl_2.2N_2H_5Cl.0{\cdot}5N_2H_4$. Zn gives $ZnI_2.2N_2H_4I.0{\cdot}5H_2O$, while the similar salt of Cd is anhydrous. In many respects these salts naturally show much analogy with the corresponding NH_4 salts. An interesting derivative of hydrazoic acid with cyanogen has been prepared by Darzens (*Compt. Rend.*, cliv., 1232). By the action of NaN_3 upon cyanogen bromide, $N{\equiv}C.N_3$ is formed, called by Darzens carbon pernitride, but better cyanogen trinitride (or hydrazoate). CN_4 is a colourless oil which crystallises in needles melting at 36°, and is soluble in most organic solvents. Slightly volatile in a vacuum, it begins to decompose at 70° and explodes at 170° with great violence. It is exceedingly sensitive to shock, but in a perfectly pure condition can be preserved a long time. It readily undergoes polymerisation, forming a solid which is insoluble in ether and not exploded by a blow. The aqueous solution of CN_4 readily hydrolyses to the acid, $N_3.COOH$, which in turn decomposes into HN_3 and CO_2.

Three papers have appeared from Ephraim (*Ber.*, xliv., 3405, 3414, 3416) on substituted phosphoric acids. Owing to hydrolysis the only tetrathiophosphate hitherto prepared is that of sodium. It is possible that the anion of this salt, $PS_4{-}{-}{-}$, hydrolyses, but more probable that it must be considered as decomposing, $2Na_3PS_4 \rightleftharpoons 2Na_2S + P_2S_5$, the P_2S_5 then hydrolysing. Antagonising this reaction by the use of a large excess of alkaline sulphide with a minimum of water, Ephraim was able to prepare from P_2S_5 the tetrathiophosphates of potassium, ammonium, and barium, but with strontium only a hydrogen trithio-salt, $Sr_3H_6(PS_3O)_4.aq$. Ephraim protests against these compounds being called *sulpho* phosphates, since a *sulpho*-compound should be derived from SO_3H. They should be called thiophosphates, *thio* being used for those compounds in which *bi*valent sulphur replaces oxygen. For the different acids of this series he proposes the names: for $(HO)_3P:S$, *thion*-phosphoric acid; for $\begin{matrix}(HO)_2\\HS\end{matrix}P:O$, *thiol*-phosphoric acid; for $\begin{matrix}HO\\(HS)_2\end{matrix}P:O$, *dithiol*-phosphoric acid; and for $\begin{matrix}(HO)_2\\HS\end{matrix}P:S$, *thion-thiol*-phosphoric acid. When the lower oxides, P_4S_3 and P_4S_7, react with sodium sulphide, the same product seems to be formed, though with differing amounts of water of crystallisation. The formula corresponds to $Na_3PS_3.aq.$, but the compounds are not thiophosphates, since after removal of the sulphur by water a compound is left which reduced permanganate. In spite of the fact that the acid is tribasic (trithiophosphorous acid should be dibasic), Ephraim is inclined to think the compound is sodium trithiophosphite. When P_4S_7 is used in its preparation there is an evolution of spontaneously combustible phosphine, but with P_4S_3 only ordinary phosphine and hydrogen. By the treatment of the compound $P\!\begin{matrix}\nearrow OC_6H_5\\\equiv Cl_2\end{matrix}$ with sulphur there is formed $S:P\!\begin{matrix}\nearrow OC_6H_5\\\equiv Cl_2\end{matrix}$, and this with ammonia gives a beautifully crystallised and stable phenyl ester of diamino-thion-phosphoric acid, $S:P\!\begin{matrix}\nearrow OC_6H_5\\\equiv(NH_2)_2\end{matrix}$. The free acid can be obtained from this by saponification with solid KOH and acidification, but not in a pure condition. The chloride of the diphenylester of phosphoric acid, $O:P\!\begin{matrix}\equiv(OC_6H_5)_2\\\swarrow Cl\end{matrix}$ gives with hydrazine the ester of hydrazino-phosphoric acid, from which salts of this acid, $O:P\!\begin{matrix}\equiv(OH)_2\\\swarrow NH.NH_2\end{matrix}$, can be prepared, as well as those from the monophenyl ester. The free acid is unstable but can be kept in alkaline solution. More than ten different salts of these two acids are described.

Group VI.—A number of studies of peroxy-salts have appeared during the year, among them two by Riesenfeld and Rau on the percarbonates (*Ber.*, xliv., 3589, 3595), who recognise three types of these compounds, the carbonate with H_2O_2 of crystallisation, the true percarbonates Na_2CO_4, and those of the $Na_2C_2O_6$ type. The compounds $Na_2CO_3.H_2O_2.0{\cdot}5H_2O$ and $Na_2CO_4.1{\cdot}5H_2O$ (types 1 and 2) are isomeric, but show even in solution different chemical characteristics. D'Ans and Frederich (*Zeit. Anorg. Chem.*, lxxiii., 325) have used as a method of preparing peroxides of alkalis and alkaline earths the solution of the metal in an ethereal solution of H_2O_2.

Quite an extensive study of aminosulphonic acid and its derivatives has been made by Hofmann (*Ber.*, xlv., 1394, 1731). The use of the acid, which crystallises pure and anhydrous, out of a not too concentrated solution of hydroxylamine hydrochloride which has been saturated with sulphur dioxide, is suggested as a standard for acidimetry. The acid is not hygroscopic and can be

accurately weighed. It can be titrated in o·1 *N* strength against o·1 *N* KOH with phenolphthalein or methyl orange, against o·1 NH_3 with rosolic acid, and against o·01 BaOH with phenolphthalein. In all these cases it gives accurate acid values. The o·1 *N* solution is hydrolysed by 90 minutes boiling to the extent of 38·5 per cent, and 88 per cent in 11 hours. At 40° the hydrolysis is very slow, and at 15° not recognisable at the end of a week. Since the hydrolysis gives rise to ammonium hydrogen sulphate it does not affect the acid value, but owing to the presence of ammonium cannot be used with phenolphthalein as an indicator. Aminosulphonic acid is an excellent reagent for the preparation of aryl-sulphuric acids and phenol-sulphonic acids. An interesting series of salts is described in which the hydrogen of the NH_2 group is more or less replaced by Hg, Ag, or Au, as for example, $Hg:N.SO_2OK$, $AgHN.SO_2OK$, and $Au_2(N.SO_2OK)_3$.

The work of Gutbier on chloro- and bromo-tellurates has been continued (*Journ. Prakt. Chem.*, [2] lxxxvi., 150) by the preparation of a large number of these salts of organic bases, chiefly belonging to the aromatic series. The chlorotellurates are all yellow and the bromotellurates red. All are anhydrous and not one crystallises in the regular system. To these must be added (*Ibid.*, lxxxv., 321) a large number of bromo-selenates, both of the alkali metals, which are all octahedral, and of alkylammoniums. Hexabromoselenic acid, H_2SeBr_6, was prepared by acting on finely divided selenium in concentrated hydrobromic acid with bromine. On adding the bromide of the base, the anhydrous bromoselenates crystallise out. They are all easily hydrolysed, and the organic salts do not crystallise in octahedral form.

Group VII.—Salvadori (*Gazz. Chim. Ital.*, xlii., [1] 458) has investigated the hydrates and ammoniates of the perchlorates of the bivalent metals. The typical hydrate, as would be expected, is $M''(ClO_4)_2.6H_2O$, where M'' is Co, Ni, Mn, Cd, Zn, or Cu. A tetrahydrate is also formed in each case except that of Co, and with Cu the tetrahydrate is the stable form. Hexa-ammoniates, $M''(ClO_4)_2.6NH_3$, are formed with Co, Ni, and Cd, and tetra-ammoniates with Co, Cd, Zn, and Cu. Mn and Cu, while not giving hexa-ammoniates, form mixed compounds of the hexa-type, $Mn(ClO_4)_2.5NH_3.H_2O$ and $Cu(ClO_4)_2.4NH_3.2H_2O$. Cu has also a strong tendency to form basic perchlorates. An interesting case is that of five cobalt perchlorates, with respectively $6NH_3$, $4NH_3$, $3NH_3$, $4NH_3.2H_2O$, and $3NH_3.3H_2O$, which readily pass from one into the other on increasing or decreasing the vapour pressure of water and ammonia surrounding them. These are all strongly coloured, red, blue, or green, but another cobalt perchlorate exists, $Co(ClO_4)_2.2NH_3.2H_2O$, which is yellow, more stable than the others, and seemingly of an entirely different character. Another attempt has been made to prepare perbromic acid and the perbromates (Robertson, CHEM. NEWS, cvi., 50) and again unsuccessfully. Even up to 250°, bromine in the presence of KBr had no effect upon $KClO_4$, nor was the slightest trace of iodine given off from KIO_4 by the action of bromine. On heating $KBiO_3$ with PbO_2 the only product of the reaction was KBr. Robertson considers that in the formation of perbromic acid the vibration of the atoms within the molecule may be too great for such a system to exist. On the other hand, since both perchlorates and periodates are stable, it seems more probable that chemists have merely failed thus far to catch just the conditions demanded for the formation of the perbromates, as they have failed also to get the oxides of bromine.

Group VIII.—The colours formed by heating cobalt nitrate with various oxides, as in qualitative analysis, furnishes a perennial subject of research. Hedvall (*Ber.*, xlv., 2095) has prepared Rinmann's green in hexagonal crystals of some size (2—3 mm.²), by heating zinc oxide with cobalt carbonate to 1100° with KCl as flux. The cobalt is in bivalent form and the CoO : ZnO ratio is 1 : 4·8, or perhaps 1 : 5. All this, however, does not have any bearing on the vital question as to whether, in these crystals, one has to do with a chemical individual or only a solid solution. A little more progress seems to be made by Burgstaller (*Chem. Zentr.*, 1912, II., 1523), who, noting the fact that the colours in question are blue, red, or green, considers that we are dealing in the blue and red with solid solutions which show the usual colours of cobalt in solution. In the green with ZnO we have blue on a substratum of yellow. While ZnO is white at ordinary temperatures, when heated it passes into a yellow modification, and it seems that in the presence of CoO the reversal into white on cooling is prevented. If this theory is true it would seem possible by carefully choosing conditions to obtain a blue colour with zinc. Burgstaller's ratio of CoO to ZnO in his Rinmann's green was 7·05 : 100, very different from that of Hedvall.

The work of Levy (*Proc. Chem. Soc. London*, xxviii., 91) on the cyano-platinites has confirmed Hadow's explanation of the action of bromine on these salts, except that the formula of the brown salt should be $6\,K_2Pt(CN)_4.K_2Pt(CN)_4.Br_2$, instead of 5 molecules of the unoxidised salt, as Hadow thought. Levy also oxidised the cyano-platinite by MnO_2 or PbO_2 in sulphuric acid solution, obtaining a similar compound to that obtained by the action of bromine. It thus seems that $(7K_2Pt[CN_4])$ is capable of acting as a feebly positive bivalent base. More interesting were the results obtained by oxidising the cyano-platinite with hydrogen peroxide, especially in the form of "perhydrol," when salts of the type $M'\,Pt\,(CN)_4$ (simple and double) are formed. These seem evidently to be salts of trivalent platinum, and to have the composition which may be expressed by $MCN.Pt(CN)_3$. In the discussion which followed the reading of this paper, Professor Reynolds called attention to a lithium salt in his laboratory which seemed to have the composition $Li_2Pt(CN)_5.2H_2O$, which might be $2LiCN.Pt(CN)_3.2H_2O$. Further work on these salts will be awaited with interest.

(To be continued).

THE ELECTROLYTIC REDUCTION OF IRON FOR ANALYSIS.

By J. C. HOSTETTER.

IN the view of the ease with which reductions can be carried out electrolytically, it is surprising that this subject should have been so neglected in the field of analytical chemistry. The electrolytic reduction of iron for subsequent titration seems to have attracted little attention. (The only work hitherto undertaken from this viewpoint which has come to the attention of the writer is a paper offered by H. C. Allen at the Rochester meeting of the American Chemical Society, September, 1913. The paper was read by title only, and appears not to have been published). With other ends in view, ferric salts have often been reduced by this means.

This method has been investigated to some extent by the writer for the specific purpose of subsequent titration, and has been employed by him at intervals during the past year. Since the method is entirely practicable and occasionally very desirable, it may not be amiss to call attention to the conditions to be controlled when this method is used for analytical purposes and to indicate the degree of accuracy of which it is capable.

The optimum conditions for complete reduction are primarily those which lessen the formation of oxidising compounds by the current. The most suitable electrolyte for this particular problem is dilute sulphuric acid. The temperature during electrolysis should be above 60° C. and the current density low. These conditions are unfavourable to the formation of both hydrogen peroxide and persulphuric acid (for discussion of these conditions see

Gmelin-Kraut Handb. d. Anorg. Chem., 7th Auf., Bd. 1, Abt. i., 128, 558). The amount of peroxide formed at the cathode by the action of nascent hydrogen on oxygen diffusing from the anode depends partly on the cathode material (M. Traube, *Ber.*, 1882, xv., 2434). Thus Pd, under given conditions, yields most hydrogen peroxide, Pt and Hg come next, while metals which do not readily absorb hydrogen, as Au, Ag, Zn, Cu, and Pb, yield but very little. With oxidisable anodes, such as Mg, Zn, &c., hydrogen is the sole product of the anode (*cf.*, Elsasser, *Ber.*, 1876, ix., 1818; 1878, xi., 587). In the presence of ferrous sulphate, however, the amount of hydrogen peroxide formed in the cathode chamber must necessarily be low. With the reducing action of the current any peroxide would oxidise the ferrous sulphate to ferric, and this in turn would be reduced by the current. This was tested out experimentally with 1 mgrm. of iron present and found to be true. Therefore, the time of electrolysis after complete reduction can produce no excess consumption of permanganate due to peroxide formation.

Considering the above facts, it was decided to use a gold dish of 800 cc. capacity as cathode (effective surface, 200 sq. cm.). Inasmuch as soluble anodes yield no oxidising materials in the solution, Mg and amalgamated Zn anodes were first employed. By this means the reduction is made very rapid, and the use of a porous cell around the anode is dispensed with. Since, however, it is difficult to obtain these metals free from impurity, such as iron—thus introducing a correction—the use of soluble anodes was abandoned and a Pt anode with porous cell substituted.

The use of a porous cell as an anode chamber introduces two sources of error:—(1) The absorption of iron salt by the cell itself; (2) diffusion of iron into the anode chamber, where it is immediately oxidised. The first is probably negligible since the cell "seasons" rapidly. The second is made negligible in the following manner. When the reduction is complete in the cathode chamber—as shown by test for ferric iron with thiocyanate—the current is stopped, the contents of the anode chamber poured into the cathode chamber, and, after filling the anode chamber with fresh acid, the current is allowed to run some five to ten minutes longer until the last of the iron is reduced. In this manner the iron left in the anode chamber at the end of the electrolysis is reduced to 0·1 to 0·3 mgrm. A syphon connecting the two chambers was also employed to lessen this diffusion. The large currents, however, caused so much heating in the syphon tube that its use was abandoned in favour of the above scheme.

TABLE I.—*Ferrous Ammonium Sulphate.*

Amount of salt. Mgrms.	Grms. $KMnO_4$ solution (0·1 N). Titrated directly.	Reduced electrolytically after oxidation.
3000	89·53	89·43
3000	89·44	89·40
3000	89·47	—

TABLE II.—*Electrolytic Reduction of Ferric Ammonium Sulphate Solution.*

Fe present. Mgrms.	Time of reduction. Mins.	Volts.	Ampères.	Fe in anode chamber. Mgrm.	Fe in 1 grm. solution.
570	780	2·5—8·5	0·35—8·5	0·29	0·005693
570	79	6·0—7·0	8·0—10·0	0·11	0·005696
570	109	4·5—9·0	4·8—10·0	0·22	0·005690
150	60	6·5—10	8	0·15	0·005709
570		Reduction with zinc			0·005702
570					0·005695
570		Reduction with SO_2			0·005684

Of the materials tested for suitability as porous cells, the unglazed Marquardt porcelain crucibles (20 cc.) seem to answer best. To keep spray from the anode out of the cathode chamber, the top of the crucible is covered with a funnel of the same diameter. The anode lead is brought down through the stem. The funnel is clamped over the crucible with a frame of glass rod; tension is secured with rubber bands. Oxygen escapes through a lateral hole in the funnel stem. The anode is of Pt foil with an effective area of some 28 sq. cm.

The Method.—The ferric (sulphate) solution (volume 300 cc.) is placed in the gold dish (cathode) and 10 cc. sulphuric acid (1·84) added. The anode chamber is filled with acid (1 : 30), the anode inserted, and electrolysis started. The temperature is raised to 80° C. The current employed is about 8 ampères, while the voltage drop across the cell is 8 volts. Under these conditions 0·5 grm. iron is reduced to the ferrous condition in sixty to seventy minutes. After a drop test with thiocyanate shows that reduction in the cathode chamber is complete the current is stopped, the anode chamber acid is added to the main solution, and, after re-filling the anode chamber, the electrolysis is continued ten minutes. At the end of this time the cathode liquid is titrated with permanganate.

It will be seen that the method as carried out is not particularly rapid. On the other hand, its favourable features are:—(1) Nothing is introduced into the solution that may carry impurity; and (2) conditions need be defined only within wide limits. The accuracy of the method can only be determined by more extensive comparison with reductions by other methods. The precision attainable under the best conditions is shown in Tables I. and II. Under ordinary conditions a precision of better than 1 part in 200 or 300 can not be expected until after the method has been more completely developed.—*Journal of the Washington Academy of Sciences*, iii., No. 16.

THE

PREPARATION OF SELENIC ACID AND SODIUM SELENATE FOR USE AS REAGENTS IN THE DETERMINATION OF BROMINE IN HALOID SALTS.

By PHILIP LEE BLUMENTHAL.

SELENIC acid and sodium selenate have been proposed in a previous paper from Kent Chemical Laboratory, Yale University (Gooch and Blumenthal, *Am. Journ. Sci.*, xxxv., 54) as reagents for the qualitative elimination of bromine, in determinable form, from haloid salts. These reagents when made by ordinary methods (Gmelin-Kraut, "Handbook," *Anorg. Chem.*, 1907, i., 769) may contain contaminating material likely to be objectionable. The following methods have therefore been devised for the preparation of these reagents in such condition that any foreign material remaining in them shall not interfere with the success of the analytical process.

Selenic Acid.

The method proposed for the preparation of selenic acid depends upon the action of nitric acid and potassium bromate upon selenious acid, the bromic acid formed reacting with the selenious acid according to the following equation: $3H_2SeO_3 + HBrO_3 = 3H_2SeO_4 + HBr$. Further action of the bromic acid breaks up the hydrobromic acid, according to the equation $HBrO_3 + 5HBr = 3Br_2 + 3H_2O$. Upon evaporating the solution to low volume, a second liberation of bromine accompanied by nitrogen oxides takes place, apparently according to a reaction like the following:—$2HBrO_3 + 2HNO_3 = 2H_2O + Br_2 + 2NO_2$. The free bromine and the nitrogen oxides are, of course, easily volatilised. The preparation of selenic acid based upon these reactions was put to the test as follows:—

Preliminary Test.—Selenious acid was prepared by dissolving elementary selenium in nitric acid, and evaporating the solution to dryness. The crude selenious acid so

obtained was sublimed from manganese dioxide according to the method used by Norton (*Am. Journ. Sci.*, [4], vii., 290), and the thin needle-like crystals were bottled as rapidly as possible. A solution convenient for use was made by dissolving 2 grms. of the purified selenium dioxide in 200 cc. of water and a portion of 20 cc., containing 0·1 grm. of the dioxide, was used for each test. To each portion contained in an Erlenmeyer flask were added 10 cc. of 1·1 nitric acid and a little potassium bromate, and this solution was evaporated to a low volume. When barium nitrate was added to the concentrated solution, and the free acid nearly neutralised with ammonium hydroxide, white barium selenate was precipitated. Though impure on account of its tendency to occlude foreign material, this precipitate proved to be practically free from selenious acid.

Preparation of the Reagent.—To 10 grms. of selenium dioxide dissolved in 75 cc. to 100 cc. of water were added 6 grms. of potassium bromate and 4 cc. of strong nitric acid. This mixture was heated on the water-bath until perfectly colourless. After the second evolution of bromine, which occurred when the volume was quite low, a little more bromate was added to decompose the excess of nitric acid, and the heating was continued. When the addition of a crystal or two of bromate caused no further evolution of bromine, the colourless solution was made slightly ammoniacal, heated to the boiling-point, and treated with a hot dilute solution of barium nitrate. The precipitated barium selenate, after settling, was filtered with suction, washed thoroughly with hot water, and finally transferred to a large crucible and dried at low redness. The weight of this product was about 25 grms., while the theoretical amount obtainable from the selenious acid taken was about 25·1 grms. After weighing, the selenate was treated in a porcelain crucible with 5 cc. of strong sulphuric acid (sp. gr. 1·8°) and some 20 cc. of water. The pasty mass so obtained was heated about two and one-half hours on the water-bath, and finally diluted, filtered, and washed. The filtrate and washings were made up to 1 litre, and an aliquot was taken for analysis by the method of Pierce (*Am. Journ. Sci.*, [4], i., 416). This analysis showed about 94 per cent of the selenium taken to be present. From the determination of the selenious acid present by the method of Gooch and Clemons (*Ibid.*, [3], l., 51) it was found that 85 per cent of the selenium was present as selenic acid, the presence of selenious acid in the final product being due in this case to the fact that the barium precipitation was made in alkaline solution, under which conditions barium selenite is also precipitated. The total yield of selenic acid was 78 per cent of the theoretical. Later experiments have shown that the contamination by selenious acid may be to a large extent avoided by precipitating while the solution still contains free nitric acid.

Sodium Selenate.

The preparation of sodium selenate, to be used with sulphuric acid in place of free selenic acid, was also investigated.

Preliminary Test.—Elementary selenium (1 grm.) was fused in platinum with sodium peroxide (2 grms.) and sodium carbonate (6 grms.). The mass, after dissolving in water and filtering, barely bleached a few drops of dilute permanganate, showing that the selenium had been oxidised almost completely to selenic acid, only a little selenious acid remaining.

Next, the finely-powdered metal (1 grm.) was fused with sodium peroxide (5 grms.) in a nickel crucible, and after cooling, the melt was partially neutralised with sulphuric acid to facilitate the analysis, and filtered. The filtrate and washings were made up to 100 cc., and 10 cc. of this solution were analysed by the method of Gooch and Scoville (*Am. Journ. Sci.*, [3], l., 402). Two analyses showed the yield to be fairly quantitative and suitable for the analytical elimination of bromine.

Preparation of the Reagent.—In utilising the method on a larger scale, about 105 grms. of powdered selenium and 500 grms. of sodium peroxide were thoroughly mixed and fused in charges containing 10 grms. to 15 grms. of selenium, nickel crucibles being employed. The reaction was rapid, and a few minutes' heating over a Bunsen burner sufficed to bring the mass to liquid condition. After cooling, the crucible was placed in a beaker of cold water, and covered with a watch-glass to avoid loss by spattering. The melt dissolved with great evolution of heat, and cold water was added from time to time to prevent boiling. Some finely-divided material remained floating in the strongly alkaline liquid. A slight green colour, probably due to the solution of small amounts of nickel, was also noticed. The solution could not be filtered through paper, and a platinum cone, lined with asbestos, was utilised, although the process was exceedingly laborious. The opaque filtrate consisted chiefly of sodium selenate and sodium hydroxide, with some sodium carbonate due to contact with the air.

In order to purify the selenate from sodium hydroxide, the attempt was first made to remove the latter by shaking the solution with alcohol. This procedure was found to have several disadvantages. The amount of time involved, the inconvenience of handling large quantities of strongly alkaline solution, and the not inconsiderable amount of carbonate formed, all militate against the process. But the greatest disadvantage lies in the fact that the dissolved carbonate and selenate of the lower aqueous layer are very difficultly crystallised. The successful method of purification ultimately developed consisted in evaporating the alkaline liquid to a pasty condition over a free flame, and removing as much caustic alkali as possible by continued extraction with alcohol which had been distilled from lime (97 to 99 per cent pure). The extraction was hastened by warming on the steam-bath, but in this latter treatment red amorphous selenium was formed by reduction of the solution. Six or eight extractions sufficed to remove most of the hydroxide.

The residue, consisting chiefly of sodium selenate and sodium carbonate, could not be crystallised from water. It was found necessary to convert the carbonate to sulphate in order to obtain crystallisable material, and after careful neutralisation with sulphuric acid, the mixture of sulphate and selenate was crystallised by repeated evaporations. The sulphate tends to crystallise first, and a partial separation may be accomplished in this manner. The mixed crystals of sodium selenate and sulphate first obtained were quite efflorescent, but on warming and evaporating to greater concentration, crystals of a lower order of hydration were obtained. The selenate and sulphate can also be thrown out by alcohol, but this method was not satisfactory and was discarded.

The several crops of crystals were combined, filtered on a Buchner funnel with suction, well-drained, and finally the mass was heated to 108° C. for some hours, whereby most of the water was driven out, and a mixture of nearly anhydrous sodium salts was obtained. Analysis of the mixed product showed it to average about 65 per cent of selenate, and the total yield of sodium selenate was about 58 per cent of the theoretical amount. Considerable material was lost in the preliminary attempts at purification, in the tests made from time to time, and in the mother-liquor from the crystallisations.

This material thus prepared is serviceable for immediate use with sulphuric acid in the method proposed for the separation of bromine and chlorine, and no attempts were made to separate the sulphate and selenate completely. In view of experience obtained in this work, it seems probable that by rapidly evaporating the filtered solution of selenate and hydroxide over a free flame, and rapidly extracting the residue with absolute alcohol, the carbonate formation may be, to a large degree, inhibited. This, of course, reduces the amount of sulphate ultimately formed, since the greater part of the alkali, excepting the carbonate, is removed by the alcohol treatment. The resulting aqueous solution,

containing a small amount of sulphate, but no selenite, can be purified fairly well by fractional crystallisation, as the selenate is more soluble in water than the sulphate.

It is to be noted that sodium selenate may also be prepared by fusing with sodium carbonate the barium selenate obtained in the process previously described for making selenic acid, the amount of carbonate taken being less than that required to decompose the barium salt completely. Upon extracting the product with water the sodium selenate dissolves, and may be crystallised from the filtered solution.

The processes described afford easy means for preparing selenic acid and sodium selenate in such condition that, though these products are not pure, they are suitable for use in the quantitative elimination of bromine from haloid salts according to the methods to which reference has been made. —*American Journal of Science*, xxxv., p. 93.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

The Burns from the X-rays.

A somewhat prolonged manipulation of the X-rays occasions too often, alas! very serious accidents that are sometimes fatal. As a means of protection it has been considered advisable to use gloves of a special kind absorbing 60, 75, and even 80 per cent of the X-rays. But the hard rays were hardly ever absorbed. Dr. Maxime Menard, head of the service of radiology at the Cochin Hospital, has just devised an efficacious method of protection against the attacks of the X rays. A special kind of chest or cupboard, composed of three panels, lined inside with a sheet of lead, of which the minimum thickness is 4 mm., protects the specialist in radiology. Crookes's tube producer of the Röntgen-rays and the patient who is to undergo the treatment of the radiations are placed inside this cupboard. The protecting gloves are formed of a rubber tissue in which have been incorporated salts of lead and sulphate of baryta. These metallic salts totally absorb the X-rays when in suitable proportion. The thickness of the tissue does not exceed 4 mm. The gloves are rather heavy, but they can nevertheless be easily managed. The experiments made by Dr. Menard in the most variable conditions have shown that the protection of the radiologist and his assistants against the X-rays was absolute.

The Protection of Buildings against Lightning.

The electrical atmospheric discharges to which a building is exposed are of two sorts. The first results from the gradual increase of potential between the cloud and the building; when this difference is sufficient to overcome the critical resistance of the air interposed, the discharge takes place; this discharge, generally oscillating, is regulated by the known laws of electricity relating to resistance, inductance, and capacity. The second sort is a violent secondary discharge which is produced in the neighbourhood; it is hardly influenced by ordinary lightning conductors, and to protect the building with them the roof would require to be largely covered with metal. Lightning discharges are oscillating, and the oscillations are exceedingly frequent, from 100,000 to perhaps several millions of periods to the second. Now the electric constants of these conductors are entirely different to those frequencies to what they are normally; the impedance especially is considerable. Little is known concerning the electrical conditions of atmospheric discharges. Generally the discharges between the clouds and the earth are of a very high voltage, and consequently put a considerable energy in movement. This energy is transformed partly into Joule heat and partly into electric radiation emitted in the form of waves. The fraction of energy thus radiated depends upon a crowd of circumstances, particularly it increases with the frequency. If the discharge takes place between the cloud and a thin rod of copper, for a frequency of a million periods, it is calculated that the quantity of energy radiated may be fifty times greater than that transformed into heat. Nevertheless there is always uncertainty as to the amount of frequency. If it is admitted that the discharge after having reached the rod of the conductor is influenced by the characteristics of this rod, the length of the rod for a height of 15 metres would give frequencies of the order of five millions. If, on the contrary, it is considered that the length of the wave is regulated by the distance of the cloud from the earth, the frequency would be much lower, 250,000 periods, for example, for clouds at 600 metres. In order to render good service, the lightning conductors must be well installed. If not they are more dangerous than useful. A lightning conductor of great height and with some defect (such as wire broken at one point, badly joined, or badly set into the ground) may attract dangerous discharges on to the house. It is necessary to supply the building that is to be protected from lightning with a large number of rods, which seems to assure the best outlet for the secondary discharges; six for a house of 30×15 metres are not too many. These rods must be placed outside the house, and as much as possible isolated from all the metallic canalisations of the building. In town it is good to employ copper rods for lightning conductors. In the country galvanised iron may be employed; it is advisable to give it the form of a cylinder or a tube.

Distillation of Coal at a Low Pressure and Low Temperature.

M. A. Pictet and M. Bouvier, of Geneva, have just made a series of interesting experiments. By distilling coal in vacuum, without exceeding 450°, these two *savants* have collected a cold condensed liquid (1·5 per cent of the weight of the coal) and a tar (4 per cent), and no ammonia. This tar, called vacuum tar, is very different from ordinary tar. It is light brown, and does not contain any phenol, but merely bases. After a washing with alkali and acids, if it is made to undergo another distillation, slightly fluorescent liquids appear, very much resembling petioles, then products of turpine and menthol. The oxidation of these products only give acids of an oily nature. In these tars we find neither naphthaline nor anthracine, nor any aromatic body. If this vacuum tar is passed through a red-hot tube then there will appear:—(1) Lighting gas; (2) strongly ammoniacal substance; (3) ordinary tar, charged with phenol, benzine, and anthracine. The pyrogenous distillation of coal is then made in two operations, and the formation of the latter products is preceded by the formation of vacuum tar. This study is of the greatest interest as far as concerns the possible genesis of natural petioles.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 3rd inst., the Duke of Northumberland, President, in the Chair. It was announced that the Eighty-eighth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. H. H. Turner, D.Sc., D.C.L., F.R.S., Savilian Professor of Astronomy in the University of Oxford, his title being "A Voyage in Space." The Lectures will be experimentally illustrated, and the subjects are as follows:—"The Starting Point—Our Earth," Saturday, December 27, 1913; "The Start through the Air," December 30; "Journeying by Telescope," January 1, 1914; "Visit to the Moon and Planets," January 3; "Our Sun," January 6; and "The Stars," January 8. The lecture hour is 3 o'clock.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*Studies in Heredity.* II. *Further Experiments in Crossing the British Species of Sea Urchins.*" By Prof. E. W. MacBride, F.R.S.

In this paper the results obtained two years ago and communicated to the Society are confirmed and extended. The hybrid produced by fertilising the egg of Echinus with the sperm of Echino-cardium is described. This hybrid was not obtained two years ago. The effect of foreign sperm in producing cytolysis on an egg is described, and it is also shown that an egg may become totally unreceptive for foreign sperm whilst it is still perfectly capable of being fertilised with the sperm of its own species.

"*Soil Solution and the Mineral Constituents of the Soil.*" By A. D. Hall, F.R.S., W. E. Brenchley, and L. M. Underwood.

"*Synthesis by Sunlight in Relationship to the Origin of Life.—Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy.*" By Prof. B. Moore, F.R.S., and T. A. Webster.

"*Trypanosomes causing Dourine* (*Mal de Coït or Beschälseuche*). By B. Blacklock, M.D., and W. Yorke, M.D.

"*Postural and Non-Postural Activities of the Mid-Brain.*" By T. G. Brown.

"*Nature of the Coagulant of the Venom of* Echis carinatus." By J. O. W. Barratt.

"*Morphological Studies in the Benzene Series.* IV. *The Crystalline Form of Sulphonates in Relation to their Molecular Structure.*" By E. H. Rodd.

"*Structure of the Diamond.*" By Prof. W. H. Bragg, F.R.S., and W. L. Bragg.

"*Electric Discharge Phenomena in Rotating Silica Bulbs.*" By Hon. R. J. Strutt, F.R.S.

"*Origin of Thermal Ionisation.*" By J. N. Pring.

"*Refraction and Dispersion of Gaseous Nitrogen Peroxide.*" By Clive Cuthbertson and Maud Cuthbertson.

The New Council.

The following is a list of those who have been recommended by the President and Council of the Royal Society for election into the Council at the anniversary meeting on December 1 :—

President—Sir William Crookes, O.M., F.R.S.

Treasurer—Sir Alfred Kempe, M.A., D.C.L.

Secretaries — Sir John Bradford, K.C.M.G., M.D., D.Sc., and Prof. Arthur Schuster, Sc.D., Ph.D.

Foreign Secretary — Dukinfield Henry Scott, M.A., Ph.D., LL.D.

Other Members of the Council—The Right Hon. Arthur James Balfour, D.C.L. ; Prof. William Maddock Bayliss, D.Sc. ; Frank Watson Dyson, LL.D. ; Henry J. H. Fenton, Sc.D. ; Prof. William Gowland, D.Sc. ; Frederick Gowland Hopkins, D.Sc., M.B. ; Sir Joseph Larmor, D.Sc. ; Prof. Charles H. Lees, D.Sc. ; Prof. Ernest William MacBride, D.Sc. ; Prof. Grafton Elliott Smith, M.D. ; Prof. James Lorrain Smith, M.D. ; Sir John Thornycroft, LL.D. ; Prof. William Whitehead Watts, Sc.D. ; Alfred North Whitehead ; Charles T. R. Wilson, B.Sc. ; Arthur Smith Woodward, LL.D.

PHYSICAL SOCIETY.

Ordinary Meeting, October 24th, 1913.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper entitled "*The Ice Calorimeter, with Remarks on the Constancy of the Density of Ice,*" was read by Mr. Ezer Griffiths.

The primary object of the work was the re-determination, by an electrical method, of the constant of Bunsen's ice calorimeter. The heat was supplied by a manganin coil wound on a mica rack which fitted the interior tube of the calorimeter, and the results are based on determinations of E.M.F. and resistance. The current was adjusted so that the difference of potential at the ends of the heating coil was exactly equal to the E.M.F. of a number of standard cadmium cells in series.

The conditions were varied as much as possible. Thus the rate of energy supply in the fastest experiments was more than seven times that in the slowest.

Errors due to progressive freezing or thawing of the ice mantle were greatly diminished by suspending the calorimeter within a transparent vacuum vessel of cylindrical form, the stem and capillary of the calorimeter projecting through a rubber stopper, and the vacuum vessel being completely embedded in powdered ice.

The mean value of the calorimeter constant was found to be 15 486 mgrms. of mercury per mean calorie.

The Constancy of the Density of Ice. Various observers have advanced evidence tending to show that the density of ice at 0° C. is not a definite constant. A consideration of their work leads to the conclusion that the small variations of density found for different samples might be simply due to the presence of occluded water or an amorphous modification cementing the ice crystals together.

The value (80·30) of the latent heat of fusion of ice, calculated from the ice calorimeter, supports this view, as it is higher by about 0·7 per cent than the value obtained by direct determinations with ice in bulk.

Discussion.

Prof. H. L. Callendar noted with pleasure that the author had very closely verified Dieterici's value, using an entirely different method. He had had occasion to look into Dieterici's determinations in connection with the specific heat of water, and thought them very reliable. They agreed very closely indeed with the results obtained by Dr. Barnes and himself by the continuous electric method. The most uncertain element in Dieterici's work was the thermal capacity of his silica bulb, which amounted to about 25 per cent of the whole. The extreme uncertainty of the calculation of latent heat from the volume changes on melting was not, perhaps, sufficiently realised. The calculation depended on the *difference* of the specific volumes of ice and water, so that any error in the value assumed for the density of ice seriously affected the value obtained for L. Thus the author, taking Vincent's result for the density of ice (=0·9161 grm. per cubic centimetre), had calculated L=80·3 *mean calories*, whereas, if 0·9167, the density as given by Barnes, had been assumed 79·5 (approx.) would have been obtained for the latent heat.

Dr. J. A. Harker mentioned a possible error due to the suction of mercury at atmospheric temperature, through a capillary of varying temperature, into the body of the calorimeter. Was the author's method of getting rid of "drift" superior to the method of putting one calorimeter inside another and larger one, and, by varying the pressure on the ice in the second one, adjusting its temperature until the "drift" was zero ? He had at one time tried glacial acetic acid instead of ice. It had the advantage that when heat was supplied mercury was pushed out instead of sucked in. Also the transition temperature was between 16° C. and 17° C., and the constant was about 30.

Mr. F. E. Smith referred to the question of the leads to the coil. If they were too thick too much heat was conducted along them ; if too thin too much heat was pro-

duced in them by the current. If the cross-section was assumed to be 2 sq. mm. then the resistance of a pair of manganin leads, each of which was 25 cm. long, would be 0·1 ohm. Since the heating coil was of 20 ohms resistance it followed that the heat produced in the leads was 0·005 times that produced in the coil. This heat was not accounted for in the calculations, and he would be glad if Mr. Griffiths would state what became of it. In his opinion much of it passed into the oil in the calorimeter. The experiments made by the author did not appear to him to indicate the magnitude of the effect, since the heat passing from the leads to the oil would be proportional to the time of an experiment and also to the square of the current used.

Prof. SILVANUS THOMPSON asked whether there was any evidence of an allotropic or amorphous form of ice. According to the theory of crystal formation by arrangements of densest packing of molecules, any amorphous form should be less dense (as is the case of fused silica as compared with quartz crystal) and its specific heat per unit mass should be greater. Was the author sure that the water used was perfectly air-free?

Prof. C. H. LEES said the author had raised his opinion of the ice-calorimeter. He would like to know where it now ranked in the author's own estimation among other instruments used for similar purposes.

The AUTHOR agreed that the calculated value of the latent heat must be accepted with reserve, as it was difficult to predict in what direction the assumed value of the density of ice might be in error. The presence of occluded water in the specimens used would make the value too high, while minute air bubbles, due to dissolved air separating out, would make it too low. He had not yet attempted the substitution of other substances for ice. The use of glacial acetic acid would obviate the trouble at the orifice, since mercury would be ejected instead of sucked in. The heating coil was so designed that the heat generated in the leads was small. Moreover, only a fraction of this would pass into the bulb of the instrument, since the coil proper extended nearly the entire length of the inner tube. The heat generated in the leads outside the bulb would be partially absorbed by the glass stem and the air surrounding the leads. The slight conduction by the glass stem and leads down to the bulb would cause a minute "drift" lasting for a considerable time after switching off the heating current. This was corrected in the manner indicated in the paper. He regarded the variation of the density of ice to be due to occluded water and not to allotropic crystallisation. He considered the water to be present as an amorphous cement binding the crystals together. In reply to Prof. Lees, he considered electrical methods, as, for example, the continuous electric method of Prof. Callendar, superior to the ice calorimeter. One advantage of the latter was, however, that there was no radiation correction.

A paper on "*An Electrostatic Oscillograph*," by Messrs. H. Ho and S. KOTO, was read by the latter.

The paper describes an electrostatic oscillograph suitable for recording very high voltages. Two vertical bronze strips pass symmetrically between two parallel metallic plates called "field plates." They are connected at their lower ends by a silk fibre which passes under an ivory pulley. An extremely small mirror is fixed to the strips. This arrangement constitutes the vibrator, which, mounted on an ebonite frame, is immersed in an oil bath. To the upper extremities of the strips are connected the terminals of a direct-current voltage of about 300. The alternating voltage to be recorded is connected to the "field plates," in parallel with which there are two oil condensers in series. The electrical midpoint of the direct-current battery is connected to a point between the condensers.

The turning moment on the strips is proportional to the product of the momentary values of the alternating-current voltage and the direct-current voltage, so that if the latter is constant, the deflection of the mirror accurately follows the variation of the former.

Oil plays an important part, not only acting as a damping agent and insulator, but increasing the sensitiveness on account of its high dielectric constant.

In cases where voltage is low, but the source of energy is so limited that a sufficient current cannot be taken to actuate the ordinary oscillograph, the electrostatic vibrator may be used by applying the voltage in question to the strips, while the terminals of a high-tension battery, or influence machine, are connected to the "field plates." The instrument may also be used for recording very small currents by replacing the oil condensers by two exactly equal resistances, which are traversed by the current.

DISCUSSION.

Mr. A. CAMPBELL thought it was a considerable advantage to be able to do without high resistances. Dr. G. W. C. Kaye had suggested to him that the instrument might be of great use in work with X-rays and in other cases where the charge was being taken from an induction coil.

Mr. R. S. WHIPPLE emphasised the commercial advantage of the instrument. High resistances were very expensive. Einthoven was the first to propose an electrostatic oscillograph, and a Belgian inventor had constructed an instrument similar in principle.

Prof. G. W. O. HOWE stated that in the two curves given the difference was assumed to be due to a "lead" in the electromagnetic instrument. Was there any actual evidence that it was not due to "lag" in the other? If the oil did produce a phase-difference, it would introduce a "lag" and give the observed effect.

Mr. E. H. RAYNER pointed out how, by suitably altering the arrangement of Fig. 8 in the paper, the instrument could be used as a wattmeter.

Mr. J. T. IRWIN said he was already aware of the device suggested by Mr. Rayner, having described it in 1907. The principal difficulty with an electrostatic oscillograph was that a very high polarising voltage is required if the zero is to be stable. The authors had reversed the process —using a small polarising voltage compared with the alternating-current voltage. Hence it is only when the alternating-current voltage is applied that a change of zero is produced. In most cases this cannot be compensated beforehand, as we do not know the value of the potential to be applied. Castor oil was not suitable for use in oscillographs, as it became acid and conducting under high voltages. Well-filtered paraffin had not this defect.

Mr. D. OWEN regretted that the paper contained so little in the way of actual work accomplished with the instrument. If one took the values stated in the paper for the inductance of the high resistances used with E.M. oscillographs, and assumed a frequency of 100 vibrations per second, calculation seemed to show that the phase-differences introduced by the use of such resistances were much too small to account for the discrepancies in the experimental curves.

Mr. G. L. ADDENBROOKE said that if castor oil free from dust and moisture were used he did not think oscillograms with the instrument would be affected perceptibly by action in the oil at 40 periods or higher. With a dry oil much lower periodicities might be used. The influence of moisture is greater with mineral oils than with castor. The dielectric strength varies almost directly with the percentage of moisture present.

Prof. KOTO, in reply, said that the frequency of the voltage used for the tests was 60 vibrations, the records being taken on a falling-plate camera. He saw no objection whatever to the use of the oscillograph as a wattmeter, as suggested by Mr. Rayner and carried out by Mr. Irwin. He stated that the oil used was that supplied by the Cambridge Scientific Instrument Co., and that from some rough measurements he had made he found it to have a specific inductive capacity of about 2. The deviation of the strips from the centre was a cause of the change of zero, as Mr. Irwin suggested, if a large polarising voltage be applied. To suppress this effect the authors made the distance between the two field plates, conse-

quently the distance between the strip and the plates, sufficiently great to make this inevitable slight deviation from the centre a very small percentage of the distance between the strip and the plates, and consequently this deviation from symmetry would cause no appreciable "out of balance" of the forces due to the polarising voltage acting upon the strips and effecting this change of zero. Referring to the effect of the oil on the phase relationship of the curves, Prof. Koto stated that he had no doubt that the curves obtained on the electrostatic oscillograph and reproduced in the paper were correct, but he intended to make a series of experiments on different oils to see whether any serious phase differences are caused by the oils having different dielectric hysteresis constants.

NOTICES OF BOOKS.

Principles of Agricultural Chemistry. By G. S. Fraps, Ph.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1913.

The greater part of this book is devoted to the consideration of the plant, its growth, its relations to the soil, and to the atmosphere, its composition, &c., while questions connected with the feeding of animals are treated rather more briefly. The author quite wisely does not attempt to explain the elementary principles of chemistry, but supposes his readers to possess a fair knowledge of them, and confines himself to the discussion of their applications to the problems of agriculture. Much of his information he has brought together from the valuable bulletins of the American state experimental stations, and although he by no means neglects the work that has been done in other countries and frequently refers to the researches carried out at the Rothamsted and Woburn stations, for instance, the book has more value for the American than for the English agriculturist, since the examples and illustrations are drawn mostly from American practice. On the other hand, the author shows marked skill in the clear summarisation of the essentials of a subject, and the terseness of the style of the text is a commendable feature.

Merck's Reagenzien-Verzeichnis. ("Merck's Index of Reagents"). Third Edition. Berlin: Julius Springer. 1913.

This index is so well known as an almost indispensable aid in analytical and microscopical work that it is doubtless supererogatory to call attention to its merits. In the third edition the arrangement of the second edition is unaltered, but the latter has been revised and considerably enlarged, and in the appendix some details of new reactions and reagents which have been published during 1912 and the present year are included.

Bewährte Arbeitsweisen der Metallfärbung. ("Tested Methods of Colouring Metals"). By Prof. Dr. Ernst Beutel. Wien und Leipzig: Wilhelm Braumüller. 1913. (Mk. 1.80).

This little book will serve as a useful laboratory guide for those who want accurate and clear directions for the colouring of metals. Only well-tested methods, and such as the author has found to be thoroughly reliable in his long experience of such work, are described, and none but the simpler processes, which can be carried out with comparatively cheap materials and without elaborate apparatus, are included. Twenty methods only are chosen for description, but they have been selected so as to be as typical as possible. Some notes are given on the chemical aspects of the operations described, but the worker who has no knowledge of science should be able to get quite satisfactory results if he follows the directions, and his needs are often taken into special consideration, as, for example, in the tables giving the common and scientific names of all the chemicals employed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 11, September 15, 1913.

This number contains no chemical matter.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 16—17, 1913.

Heat of Formation of Silicon Nitride.—Camille Matignon.—When a mixture of silica and carbon is heated to 1400—1500° in a current of nitrogen the nitride, Si_3N_4, is obtained:—$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO$. It is very difficult to determine the heat of formation of this nitride directly, but it may be calculated if a single state of equilibrium is known, and the specific heats. Employing this indirect method the author has obtained the value 159·3 cal., and although this number cannot be regarded as very accurate, it gives some indication of the order of magnitude of the heat of formation of the nitride.

Rotatory Dispersion of Free 1-Bornyl-xanthogenic Acid.—L. Tchougaeff.—A freshly prepared solution of 1-bornyl-xanthogenic acid is lævorotatory for all wavelengths of the visible spectrum, and moreover exhibits the Cotton phenomenon (abnormal rotatory dispersion), the curve passing through a maximum at about 525$\mu\mu$. If, however, the solution is allowed to stand the curve undergoes important changes. The values corresponding to the red part of the spectrum diminish, while those corresponding to the green and blue parts increase, and hence the maximum of rotation is displaced towards the violet part of the spectrum. Thus the abnormal dispersion is gradually replaced by that which is characteristic of borneol. The cause of this phenomenon is the spontaneous decomposition of the acid, according to the equation $C_{10}H_{17}OCSSH = C_{10}H_{17}OH + CS_2$.

Rotatory Dispersion of Derivatives of β-Pinene.—L. Tchougaeff and A. Kirpitcheff.—The rotatory dispersion of nopinone is much greater than that of nopinol, and thus the ketonic group is again accompanied by an abnormal exaltation of the dispersive power. The temperature exercises only a very slight influence on the values of the specific rotatory power. The absorption curve of nopinone exhibits a band the maximum being at about 3550, but nopinol absorbs only the extreme ultra-violet, and shows no characteristic band.

Preparation of Anhydrous Manganese Iodide.—F. Ducelliez.—To prepare manganese iodide the finely-divided metal is covered with dry ether, and dry iodine is dropped in. The reaction begins at once, and the ether boils; it is necessary to cool at first, but afterwards the solution is heated on the water-bath, the ether being condensed by means of a reflex condenser. If excess of metal is used the powdered iodide thus obtained is light enough to be poured off with the ether, and thus separated from the manganese. The iodide is white when freshly prepared, but it turns brown after a time; it is soluble in water, and it combines very readily with gaseous ammonia to give products which the author is investigating.

Preparation and Properties of Basic Copper Sulphate, $CuSO_4.CuO$.—Emm. Pozzi-Escot.—To prepare basic copper sulphate a saturated solution of copper sulphate in commercial formol is prepared and warmed, and potassium bisulphite is added. The bisulphite decomposes the copper sulphate, giving cuprous oxide, which then dissolves in the excess of copper sulphate and re-oxidises. Thus an abundant greenish white crystalline precipitate is obtained. The analysis of this substance gives results which agree very well with the formula $CuSO_4.CuO$. When it is heated in a glass tube it turns yellow, and then fuses to a red liquid which can be kept for some time at this temperature without undergoing decomposition. The

sulphate is insoluble in water, but warm water decomposes it slowly, giving a deposit of oxide. It dissolves immediately in dilute acids and decomposes silver nitrate solution with formation of a mixed compound. In damp air it absorbs a molecule of water and gives a green crystalline compound of formula $CuSO_4.Cu(OH)_2$.

Presence of Boron in Milk and Eggs.—Gabriel Bertrand and Henri Agulhon.—If boron is a fundamental element of the living cell it must exist in the organism from the very beginning, and hence should be found in milk and eggs. The determination of the metalloid in both substances has always given positive results when carried out by the authors, and they consider that boron should be classed with the other catalytic elements of the living cell.

Determination of Tartaric, Malic, and Succinic Acids in Wine.—Paul Dutoit and Marcel Duboux.—To determine tartaric, malic, or succinic acids by the physico chemical volumetric method the diluted solution is treated with a suitable precipitant in small quantities, and after each addition the conductivity is determined. The results are expressed graphically (conductivity as ordinates, reagent as abscissæ), and it is found that the "precipitation curve" thus obtained has a marked inflection at the point at which precipitation is complete. The best reagents to use in the case of the acids in question are the salts of barium and lanthanum. In wines the three acids must first be separated from other substances in solution, the best method being to precipitate with silver nitrate, and dissolve the precipitate in alcoholic sodium bromide or chloride. The sum of the three acids is first determined by the use of the formula $2000 \frac{X \times N}{v}$, where X = number of cc. of reagent corresponding to the point of inflection, N is the normality of the reagent, v is the volume of the solution used. Since the difference of the solubility of the malate and succinate of barium is considerable in a solution containing 60 per cent of alcohol, the same method, using barium acetate as reagent, can be applied to the determination of the tartaric and malic acids, the succinate remaining in solution. Finally, the tartaric acid is determined by using 25 cc. of the solution, 75 cc. of alcohol at 95°, 5 cc. of glacial acetic acid, and precipitating with 0·89 N barium acetate solution.

Determination of Pure Caoutchouc in Raw Caoutchouc.—R. Marquis and F. Heim,—The amount of pure caoutchouc in a raw specimen may be ascertained by dissolving in chloroform, and adding about eight times the weight of pure sulphuric acid. After shaking for three minutes two volumes of alcohol are added, and the whole is allowed to stand for some hours. The flocculent precipitate is then filtered off, washed with alcohol, dried at 100°, and weighed. Its weight is exactly equal to that of the pure caoutchouc present. The formula of the precipitate appears to be $(C_{10}H_{16})_{10}H_2O$. For the purposes of an exact analysis it is preferable to separate the resin from the raw caoutchouc before applying this method.

MISCELLANEOUS.

Lewis's Quarterly List of New Books and New Editions.—We have received the October number of the additions to Lewis's Technical and Scientific Circulating Library. It contains the books which have been published and added to the Library during the months of July, August, and September. These are not the busiest months for the publisher, and consequently the list does not contain quite so many important works as usual. The first part of the list is occupied with the additions to the medical side of the Library, while in the second, under the general heading "Scientific," will be found those on such subjects as Chemistry, Engineering, Metallurgy, Motor Cars, Technology, &c. Under the last-named, we notice the first volume of the new edition of Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes" is included. Other interesting books are Part VI. of the 3rd edition of Frazer's "Golden Bough" (under "Anthropology"), Reid's "Turbines Applied to Marine Propulsion," Butler's "Portland Cement," Brewer's "Carburation," &c. Short notes are given to the more important works, and the list should be useful to those wishing to see what has appeared during the months included on any subject they are interested in.

Royal Society of Arts.—The Society will commence its 160th Session on November 19 with an Address by the Chairman of the Council, Col. Sir Thomas H. Holdich, K.C.M.G., K.C.I.E., C.B., D.Sc. Before Christmas there will be four meetings besides the opening meeting. The first of these will be devoted to a paper by Dr. Chalmers Mitchell, on "Zoological Gardens"; the second to a paper by Mr. John Umney, on "Perfumery." At the third, Mr. Thorne Baker will read a paper on "Applications of Electricity to Agriculture," and at the last meeting before Christmas, the question of the Channel Tunnel will be brought forward by Mr. Arthur Fell, M.P. A number of papers for the meetings after Christmas have also been promised, but the dates for these are not yet arranged. Amongst them will be a lecture by Sir Sidney Lee, on "Shakespeare's Life and Works," to be delivered under the Aldred Trust, which is intended for the Promotion of Literature as well as Science. There will be five courses of Cantor Lectures. The first, by Prof. Coker, on the "Measurement of Strains in Materials and Structure," will comprise, amongst other matters, the results of his own investigations into the application of polarised light to the measurement of stresses. The second course will be by Sir Charles Waldstein, who will deal generally with the subject of "Industrial Art"; the third by Mr. Joseph Pennell on "Artistic Lithography." The subject of the fourth course will be announced later. The last will be by Mr. William Burton on "Recent Developments in the Ceramic Industry." A course of lectures will also be delivered under the Cobb Trust, established from the surplus of funds subscribed for a memorial to Mr. Francis Cobb, who died in 1901. The lecturer will be Mr. Plunket Greene, and the subject of the lectures will be "The Singing of Songs, Old and New." A course of Juvenile Lectures to be delivered as usual during the Christmas holidays will be given by Mr. Howgrave Graham, and will deal in a popular way with the subject of "Wireless Telegraphy." They will be very fully illustrated.

MEETINGS FOR THE WEEK.

TUESDAY, 18th.—Chadwick Public Lectures, 5. (The University of London, South Kensington). "The Place of the Open-air School in Preventive Medicine," by Sir George Newman, M.D.

WEDNESDAY, 19th.—Microscopical, 8. "Shell Structure in the genus Lingula, Recent and Fossil," by F. W. Chapman. "Development of an Embiid," by J. C. Kershaw.

THURSDAY, 20th.—Royal Society. "Neuro-muscular Structures in the Heart," by A. F. S. Kent. "Alleged Excretion of Creatine in Carbohydrate Starvation," by G. Graham and E. P. Poulton. "On *Medullosa Pusilla*," by D. H. Scott. "Origin and Destiny of Cholesterol in the Animal Organism—Part XI., The Cholesterol Content of Growing Chickens under different Diets," by J. A. Gardner and P. E. Lander. "Contributions to the Biochemistry of Growth—On the Lipoids of Transplantable Tumours of the Mouse and the Rat," by W. E. Bullock and W. Cramer.

—— Chemical Society, 8.30. "Interaction of Sodium Amalgam and Water," by H. B. Baker and L. H. Parker. "Action of Variously Treated Waters on Sodium Amalgam," by L. H. Parker. "Some Derivatives of Oleanol," by F. Tutin and W. J. S. Naunton. "Some Derivatives of Phorone," by F. Francis and F. G. Willson. "Porosity of Iron," by W. H. Perkin. "Bleaching Action of Hypochlorite Solutions," by S. H. Higgins.

THE CHEMICAL NEWS.

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SOME CURIOUS ATOMIC WEIGHT RELATIONS.

(A Supplementary Note).

By F. H. LORING.

The report from France* (Chem. News, cviii., 322) that gallium is present in commercial aluminium may be of interest in connection with Sir J. J. Thomson's positive rays. Quoting from the *Roy. Soc. Proc.*, 1913, A, lxxxix. (Bakerian Lecture), Thomson says:—"On the plate on which the helium line was strongest—the salt was KI—I could see a very faint line correspoding to an atomic weight 35 or thereabouts. I should have thought this was due to a trace of chloride among the potassium iodide, except for the fact that when KCl was substituted for KI this line was not strengthened. I have not yet been able to get this line strong enough to measure it with sufficient accuracy to decide whether the particle producing it has an atomic weight exactly equal to the difference of the atomic weight of potassium and helium" (p. 19).

If gallium is widely distributed in nature, as indicated, its presence in a vacuum tube would not be strange. It has physical properties closely resembling mercury, and it might, if I interpret Sir J. J. Thomson's experiments aright, carry a double charge (compare mercury), and in consequence have an apparent atomic weight of half 70. Of course there might be an inactive gas of an atomic weight near to that of gallium (see *Phys. Zeit.*, 1911, xii., 111), but this possibility seems very remote.

Since gallium is in question here, it will be of some interest perhaps to consider its atomic weight. This element does not fall into line with the other elements in my scheme (Chem. News, 1909. xcix., 150), and, from the tabular arrangement given, it should apparently fall on the curve with bromine. This would entail a value of 71·37, which would find a place in a further extension of the scheme cited (see Chem. News, c., 281), and this value (taken as 71·33) together with the fact that the element in question is allied to thallium, renders possible the following series:—

Atomic weights.			Differences.		
H	=	1·01*			
			7·89		
Be	=	8·90			18·66 (b)
			26·55		
Cl	=	35·45			9·33 (a)
			35·88		
Ga	=	71·33			

$$2a = b\,;\ a+b = 28.$$

* Rounded to second decimal place, the true value being close to 1·008.

It will be seen that the atomic weight of beryllium is altered slightly, and hydrogen is assumed to be sufficiently related to helium to occupy a place at the head of a series (see Chem. News, 1912, cvi., 37). In passing upwards through a Mendeleeff group to the initial member, the continuity in properties ceases, in a sense, at the first element, yet a continuation is possible with a minimum change in some properties down the *next* group, thus linking up, for example, helium with hydrogen or lithium, or group O with group I. Wrapping the Table round a cylinder, group O may be represented as group IX. In regard to beryllium, quoting from Browning ("Introduction to the Rarer Elements," 1912, p. 20):—"The compounds of beryllium closely resemble those of aluminium." The significance of these relations will be seen upon a comparative study of this series with those previously given (Chem. News, 1913, cviii., 95, 188).

The atomic weight of gallium was determined by its discoverer, Lecoq de Boisbaudran, in 1878, and it would appear that no further determination has been made. It seems reasonable, therefore, not to attach too much importance to the early measurement, especially as a comparatively recent determination of the atomic weight of mercury has yielded a value 6/10ths of a unit higher than the previously accepted figure.

If active hydrogen is eligible as an initial member in a quaternian series, then nitrogen should also be eligible. Taking N = 14·00, Cr = 52·02, Ru = 101·70, and Gd 157·21, a fairly satisfactory series may be constructed, especially when it is noted that europium from spectroscopic considerations falls between cadmium and mercury. (Dr. W. M. Hicks in "A Critical Study of Spectral Series" says:—"An attempt is made to arrange the S and D series for europium and radium. Eu is found to fit the gap between Cd and Hg and a density 12·58 deduced for it," *Phil. Trans. Roy. Soc.*, 1912, ccxii., 33). Gadolinium, which is the next element, should then fall between indium and thallium. These elements were so placed in an alternative form of Periodic Table published in the Chemical News, 1909, c., 283.

The place assigned to ruthenium seems to imply a connection with the halogens, or group VII. This is brought out in my book "Studies in Valency," 1913, though the gradient is steep, if I may so express the transition in properties of the end members taken in what might, for convenience, be termed *vertical comparison* (see Table on page 23, and comments thereon).

There appear to be seven series (some are doubtful, however) of practically four members each, which I have termed *quaternian series*. In studying the typical valency values, when all the series are so arranged or grouped that the third element in each set is progressively higher in atomic weight than its predecessor of a previous set, the total valencies or group numbers per set increase progressively down the whole series, but Ni, Fe, and Co seem to require to be assigned to the VIth group, whilst the inactive gases seem best represented as belonging to a IXth group, and hydrogen might have a group number of VII. or VIII. (see "Studies in Valency," pp. 27 and 28).

Hydrogen may be the only survivor of a series of elements perhaps differing very slightly in atomic weight. A similar idea was proposed by Palmer (see Tilden "The Elements," p. 93). This idea, moreover, is supported by the absence of eight to ten elements between hydrogen and beryllium, as indicated by the series given above, since there are ten or eleven active elements between beryllium and chlorine, and twelve between chlorine and gallium. This observation also portends that hydrogen may not be the proper member to select for the head of the series, though a better fitting one may now be extinct.

From the standpoint of radio-activity, these missing members may have been all taken up in some process of evolution, so that if the lower atomic weight elements were to disintegrate they might give back these elements. Against this idea, however, is one that hydrogen is the *alpha* and *omega* of such a hypothetical series, since, indeed, it is eligible for either end of a standard Periodic Table, according as its properties are selected for comparison with those of group I. or group VII. In other words, perhaps this series had a representation in some *urstoff*, which, "consisting of an infinite number of immeasurably small particles gradually accreting out of formless mist," gave birth to hydrogen, this being in reality Sir William Crookes's well-known conception of the "Genesis of the Elements," at least in part.

Notwithstanding these apparent regularities, beryllium and nitrogen still remain in some respects anomalous from the standpoint of my original scheme, as do some subsequent developments, so that these studies are punctuated with uncertain or discordant factors.

* Boulanger and Bardet, Academy of Sciences, Oct. 27, 1913.

A SIMPLE THERMO-REGULATOR.

By J. G. BOYD and H. M. ATKINSON.

A STOUT test-tube about 6×¾ has a good wooden cork (rubber is attacked by toluene), through which passes a narrow bore glass tube, fitting by a rubber band into the narrow part of an ordinary filtering tube.

This has a double bored stopper with two right angled glass tubes, one reaching down inside to near the top of the narrow bore tube, and ground off like the stem of a funnel, but more acutely, with a piece of carborundum.

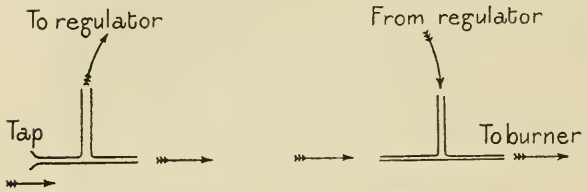

FIG. 1.—DIAGRAM OF ARRANGEMENT OF T-PIECES.

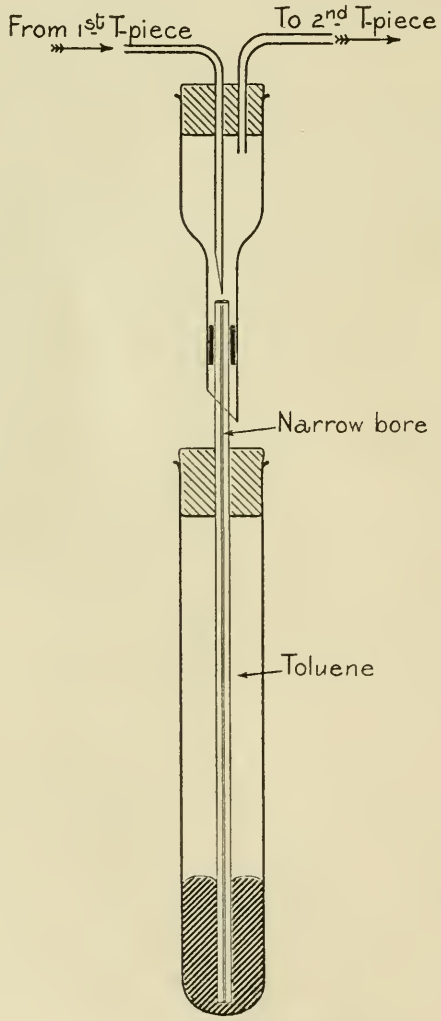

FIG. 2.—DETAILS OF THERMO REGULATOR.

The other right angle tube extends to a little below the stopper. To fit, mercury is poured into the stout test-tube, the narrow bore dipping to bottom of this, then toluene or other liquid (water serves for approximations) to fill the test-tube, and tightly corked. To ensure that mercury fills the narrow bore tube this may be gently rotated a little way up before corking, and when corked pushed down again. A few drops of mercury into the filter tube to cover the top of the capillary, and the apparatus is ready to immerse in the thermostat. By raising or lowering the gas entry tube any desired volume of gas can pass through, and hence any desired temperature.

To prevent the flame of the Bunsen burner when very low from striking back we use two glass T-pieces to provide an independent gas supply to burner controlled by a screw clip.

Technical Institute, Limerick.

RAPID ESTIMATION OF MANGANESE, VANADIUM, AND TITANIUM IN PRESENCE OF ONE ANOTHER IN PIG-IRON AND STEEL

By C. W. WRIGHT.

THE following method with care and skill is sufficiently accurate for most works purposes, but unless experience has been gained with synthetic solutions the results may be very wide of the truth.

The method is merely an extension of one given on p. 90 of "Analysis of Steel Works Materials" by Harry Brearley, on the volumetric estimation of vanadium. It is as follows:—

Dissolve 1·1 grm. in 35 cc. 1·2 nitric acid, filter off any graphite which may be present, keeping the bulk as low as possible. Add sodium bismuthate, and heat to destroy organic matter. Clear with sulphurous acid, and cool. When quite cold add an excess of bismuthate, pass through asbestos filter, wash with 3 per cent nitric acid water until clear. Add excess of N/10 ferrous sulphate, and then N/20 permanganate. So long as there is an excess of ferrous sulphate the permangate delivered at the rate of 2 or 3 drops per second disappears instantaneously, but immediately the oxidation of the vanadium commences there is a distinct retardation of the disappearing pink colour. It is almost instantaneous but quite recognisable with an experienced eye. The reading is now taken, and the titration finished to a permanent pink. In case of uncertainty the operation can be repeated any number of times by again adding ferrous sulphate and repeating the titration. From the above set of readings the vanadium and manganese can be calculated. The solution is now transferred to a comparison tube, hydrogen peroxide added, and then made up to a suitable volume not exceeding 100 cc. Meanwhile a similar steel or pig-iron which contains no Ti or V has reached a similar stage. To this is added an amount of vanadium solution exactly equivalent to that found in the sample. It is now only necessary,

Experiment	Iron present. Grms.	Per cent. Mn present.	Mn found.	V present.	V found.	Ti present.	Ti found
1.	1·1	0·33	0·32	Nil	Nil	Nil	Nil
2.	1·1	0·33	0·33	0·20	0·20	Nil	Nil
3.	1·1	0·33	0·34	0·20	0·20	Nil	Nil
4.	1·1	0·33	0·32	Nil	Nil	0·20	0·20
5.	1·1	0·33	0·33	Nil	Nil	0·20	0·20
6	1·1	0·33	0·34	0·10	0·11	0·20	0·19
7.	1·1	0·33	0·33	0·10	0·11	0·20	0·19
8.	1·1	0·33	0·34	0·20	0·20	0·20	0·20
9.	1·1	0·33	0·32	0·20	0·20	0·20	0·20
10.	1·1	0·33	0·33	0·09	0·10	0·21	0·20
11.	1·1	0·33	0·32	0·09	0·10	0·21	0·20

after addition of H_2O_2, to add standard titanium solution and compare. If the vanadium estimation is correct there should be no difficulty in comparing the colours developed. Any inaccuracy, however, will immediately declare itself by colours which will be difficult to compare. Both V and and Ti give highly coloured solutions on addition of H_2O_2, but as they are distinctly different in colour it is evident that the accuracy of the process depends on the skill and judgment exercised in determining the vanadium present. The accompanying figures show how near to the truth one can get.

THE PASSIVITY OF METALS.

By GEORGE SENTER.

The phenomenon of passivity was discovered by Keir as far back as 1790 (*Phil. Trans.*, 1790, lxxx., 359). He observed that iron, after treatment with concentrated nitric acid, had lost the property of precipitating silver from solutions of silver salts, and was no longer attacked by dilute nitric acid. The name "passivity" we owe to Schönbein, who made many important contributions to our knowledge of the subject (*Pogg. Ann.*, 1836, xxxvii., 390; xxxviii., 444; xxxix., 342; 1837, xli., 53; 1838, xliii., 103). Faraday's name is also closely associated with the early history of this subject in connection with his well-known suggestion (*Phil. Mag.*, 1836, ix., 53) that passivity is due to the formation of a coating of oxide on the surface of the metal—an explanation which still has its supporters. For a number of years after 1840 our knowledge of passivity made comparatively little progress, but about fifteen years ago a new era of rapid advance set in. This stage was initiated by the classical experimental investigations of Hittorf, who worked chiefly with chromium (*Zeit. Phys. Chem.*, 1898, xxv., 729; 1899, xxx., 48; 1900, xxxiv., 385). Among recent investigators the names of Le Blanc, Foerster, Haber, G. C. Schmidt, and their co-workers deserve special mention. The predominant share which our German colleagues have taken in the recent developments of this subject is reflected in the number of papers which they have been good enough to contribute to our proceedings this evening.

As a general rule, progress in our knowledge of any particular subject is most rapid when there is considerable divergence of opinion with regard to the interpretation of the experimental results. Such divergence of opinion has been particularly marked in connection with passivity, and even at the present time three entirely different "explanations" of the phenomenon have their supporters. The controversy has now, however, reached such a stage that a considerable measure of agreement has been reached on many points, and it is hoped that the open discussion of the subject arranged by this Society, by emphasising points of agreement as well as points of difference, may indicate the most fruitful directions for further experimental investigation, and thus contribute in no small degree to progress in a very interesting and important subject.

History of the Subject.

Keir was led to the discovery of passivity by following out an observation of Bergmann that some samples of iron are capable, others incapable, of displacing silver from its salts. One of Keir's most important observations may fittingly be described in his own words:—"I digested a piece of fine silver in pure and pale nitrous [nitric] acid, and while the dissolution was going on and before the saturation was completed I poured a portion of the solution upon pieces of clean and newly scraped iron wire into a wine-glass and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver, and was five to six times larger in diameter than the piece of iron wire which it enveloped. The action of the acid on the iron continued some little time and then it ceased, the silver redissolved, the liquor became clear, and the iron remained bright and undisturbed in the solution at the bottom of the wine-glass, where it continued during several weeks without suffering any change or effecting any precipitation of the silver.

Further experiments showed that the liquid had not lost its power of acting on *fresh* iron, although it had ceased to act on the piece exposed to it, so that the change was in the iron and not in the liquid. This led to the discovery that concentrated nitric acid alone renders iron passive, and it was further found that a sample of inactive iron regained its activity by rubbing it at a point or by bringing it in contact with a piece of active metal. The further remarkable observation was made that when a piece of active metal was placed in acid in which a piece of passive metal was lying, so that the two pieces did not touch, in a short time the passive metal became active. Keir, at the end of his paper, expresses his intention of returning to the subject in later communications, but this promise remained unfulfilled.

The next important contributor to this subject was Schönbein (*loc. cit.*). Space will only admit of a brief reference to two of his observations. In a letter to Faraday he points out that a piece of iron could be rendered passive by heating one end of it in an alcohol flame for a moment or two—not only the heated portion but the remainder of the wire is rendered passive. Further, other wires placed in contact with the partially oxidised wire are not affected in nitric acid of density 1·35 provided the oxidised end is first dipped in the acid; under ordinary conditions the wires dissolve readily in acid of this density. Later investigations appear to show that portions of wire in contact with the heated portion are not passive, but can be passivated more readily than ordinary iron (Hittorf, *Zeit. Phys. Chem.*, 1900, xxxiv., 395; Heathcote, *Ibid.*, 1901, xxxvii., 368). The contradictory results obtained with nitric acid are probably to be accounted for by the observation that under certain conditions a relately dilute acid (D = 1·250) can render iron passive (Heathcote, *loc. cit.*).

Schönbein was one of the earliest to investigate passivity by electrochemical methods, and he made the important discovery that iron could be rendered passive by making it an anode in a cell in which oxygen acids were subjected to electrolysis (so-called "anodic polarisation"). Schönbein did not himself suggest any explanation of passivity, but raised objections to the oxide theory when it was put forward by Faraday. The reasons given by Faraday in favour of his theory are as follows:—

1. All known passivity phenomena are oxidation processes.
2. Iron coated with oxide is insoluble in acids.
3. The passive condition readily disappears on polishing the metal.

His words are as follows (*cf.*, "Experimental Researches," Everyman's Library edition, p. 326):—"The iron is, in fact, as if it had no attraction for oxygen, and therefore could not act on the electrolyte present, and consequently could produce no current. My strong impression is that the surface of the iron is oxidised or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

Schönbein urged, among other objections to Faraday's theory, that iron rendered passive in acids showed no trace of a coating of oxide. To this Faraday answered that he could find no better explanation, and that he would not maintain that the coating consisted of one of the known oxides, but resembled more a condition of very fine equilibrium.

As already mentioned, Faraday's explanation of passivity was pretty generally accepted up to the commence-

* General Introduction to the Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

ment of Hittorf's investigations in 1898. The bearing of these important investigations on the nature of passivity is dealt with below. Hittorf pointed out many serious objections to the oxide theory, but did not himself put forward any very definite explanation of passivity phenomena. In connection with his observation that active chromium dissolves in the divalent form whilst passive chromium dissolves at a much more higher potential with formation of compounds containing sexavalent chromium, it has been suggested that the passive form of a metal is a different allotropic modification, much "nobler" than the active form (see below).

A third theory of passivity, the so-called "reaction velocity theory," was put forward by Le Blanc in 1900 (*Zeit. Elektrochem.*, 1900, vi., 472; 1905, xi., 9; *Boltzmann Festschrift*, 1904, p. 183), and has exercised a profound influence on the recent development of the subject. These three theories of passivity are discussed, and the arguments for and against them briefly stated in the next section.

Theories of Passivity.

The more important phenomena which have to be accounted for on any theory of passivity are as follows. The passive state is best known in connection with iron, cobalt, and nickel, but most if not all the metals may be made to assume this state under suitable conditions. Passivity may be induced by immersing the metal in an oxidising agent such as nitric or chromic acid, and in solutions of alkali hydroxides; also by anodic polarisation in a great variety of electrolytes. When the force producing passivity is removed the metal as a rule returns to the active state, slowly at first and then more rapidly, in some cases almost instantaneously. When the surface of a metal in the passive condition is scratched or rubbed, it regains its activity at once. Treatment with acids, cathodic polarisation with hydrogen, and raising the temperature all favour return to the active condition. A metal becomes much more positive (more "noble") when it changes from the active to the passive condition, and does not dissolve when the equilibrium potential is reached. On further increasing the anodic potential the metal may dissolve as a more highly oxidising ion (*e.g.*, chromium), or the current may be employed mainly or entirely in discharging anions. The rise of potential on anodic polarisation is usually slow at first, and then there is a sudden rise of considerable amount, the metal becoming almost insoluble. The nature of the anion has considerable influence. Thus the ions of oxidising acids, such as NO_3' and ClO_3' favour passivity, whilst Cl' and Br' have the contrary effect. Other phenomena met with in this connection will be mentioned in the course of the discussion of the different theories of passivity.

As already mentioned, three theories of passivity have obtained a greater or less degree of recognition :—

1. The oxide-film theory of Faraday, already referred to.

2. The valency theory of Krüger-Finkelstein (*Zeit. Phys. Chem.*, 1902, xxxix., 104) and W. J. Müller (*Ibid.*, 1904, xlviii., 577); according to this theory passivity phenomena are due to the change of a metal to the "nobler" modification.

3. The reaction velocity theory of Le Blanc (*loc. cit.*). In its most general form this theory states that passivity phenomena are due to slow rate of change (electrochemical or purely chemical) at the anode. In this form the reaction velocity theory is little more than a statement of the facts, and several special hypotheses have been put forward as regards the mechanism of the retardation. Thus we have—

(*a*) *The oxygen charge hypothesis* of Fredenhagen (*Zeit. Phys. Chem.*, 1903, xliii., 1; 1908, lxiii., 1) and Muthmann and Frauenberger (*Sitzungsber. der Kgl. Bayrischen Akad.*, 1904, xxxiv., 201). The cause of passivity is to be sought in the slow rate of reaction between the anode and the oxygen liberated there, with the result that the anode becomes charged with the gas, or, alternatively, a metal-oxygen alloy is formed.

(*b*) *The anion discharge hypothesis*, according to which the main change at the anode is not the formation of metal ions but the discharge of anions; the slow reaction of the discharged anions with the metal produces passivity. The views of Sackur (see below) are based on the assumption of a primary anion discharge.

(*c*) *The hydrogen activation hypothesis* of Foerster (*Abhandlungen der Bunsen Gesellschaft*, 1909, No. 2) and of Schmidt (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), according to which the normal condition of iron is passive and it only becomes active under the influence of a catalyst. According to Foerster the catalyst is hydrogen; according to Grave (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), a pupil of Schmidt, it is hydrogen ions.

(*d*) *The retarded ion hydration hypothesis* of Le Blanc ("Lehrbuch der Elektrochemie," 5th edition, p. 285).

Each of these theories will now be briefly considered.

The Oxide Film Theory.

The mode of action of a film of oxide or other insoluble substance in causing passivity is presumably that it coats the electrode and mechanically hinders metallic ions from entering the solution. Current can only pass when the anode potential is increased to such an extent that anions are discharged.

There can be no doubt that passivity is in some cases due to the formation of an insoluble coating. Thus when lead is anodically polarised in sulphuric acid a coating of lead sulphate forms on the anode and protects the metal against further action. It may be, however, as has been suggested by supporters of other theories of passivity (Foerster, *loc. cit.*), that such films are in some cases at least a consequence rather than a cause of passivity.

An important investigation which is often cited in favour of the oxide theory is that of E. Müller and Spitzer (*Zeit. Anorg. Chem.*, 1906, l., 321), who found that on anodic polarisation in alkali, iron, cobalt, and nickel became coated with the respective oxides and simultaneously became passive. In order to meet the objection that this might be a secondary phenomenon, they avoided the presence of the metals altogether by examining the behaviour of platinum electrodes coated with the oxides of iron, cobalt, and nickel respectively. Such electrodes on anodic polarisation in sodium hydroxide were found to behave in the same way as passive electrodes of the metals themselves, from which the conclusion was drawn that the behaviour of the latter is also due to a coating of oxide.

Haber and Goldschmidt (*Zeit. Elektrochem.*, 1906, xii., 49) cite in favour of the oxide theory the observation that iron which has been rendered passive by anodic polarisation in alkaline solution without losing its metallic lustre becomes coated with a layer of hydroxide on addition of halogen ions. Le Blanc has made similar observations with nickel anodes, but interprets them in an entirely different way. Haber and Maitland (*Ibid.*, 1907, xiii., 309) have shown that in contrast to the behaviour of alkali of moderate concentration very concentrated alkali renders iron active and that it acts by dissolving a superficial film of oxide.

The behaviour of iron electrodes on anodic polarisation has yielded results which have been adduced, more particularly by P. Krassa, in support of the oxide theory (*Zeit. Elektrochem.*, 1909, xv., 490). It is well known that iron readily becomes passive by anodic polarisation in relatively dilute alkali. Krassa now shows that in boiling concentrated alkali iron can be anodically polarised for some time without losing its activity when the current density is not too large; on continuing the polarisation the anode slowly becomes passive, but great stress is laid upon the fact that the formation of a visible coating precedes passivity. With high current density the anode at once becomes passive.

More recently Grube (*Zeit. Elektrochem.*, 1912, xviii., 189), who has made a careful investigation of the electro-

lytic oxidation of ferrocyanides, has shown that anodes of iron, nickel, cobalt, copper, lead, and silver in neutral solution of potassium ferro- and ferri-cyanide and anodes of iron, lead, silver, and zinc in alkaline solutions of the same salts, become strongly passive, and in all cases this is ascribed to the formation of an insoluble coating on the anode. In other cases there is no evidence of an insoluble coating and the passivity is ascribed to an oxygen charge which retards the liberation of cations of the metal.

The weak point in all these investigations is that they were carried out only in neutral or alkaline solution, and therefore cannot afford an explanation of passivity in general, especially in acid solution.

Objections to the Oxide Theory of Passivity.—Very serious objections to the oxide-film theory as an explanation of passivity in general have been adduced by Hittorf, Le Blanc, Fredenhagen, Foerster, and others. These will now be briefly considered.

Hittorf maintains that if the passivity of iron and chromium is to be ascribed to a coating of oxide, such oxides have not so far been discovered, since none of the known oxides possess the necessary properties. The effect of rise of temperature in destroying passivity is very difficult to account for on the oxide theory. Hittorf's so-called "experimentum crucis," whereby chromium, which was capable of decomposing hydriodic acid with the formation of the iodide and liberation of hydrogen, was rendered passive by anodic polarisation in a solution of the same acid in the absence of oxygen, is also impossible to reconcile with the oxide theory.

Finkelstein (*loc. cit.*) has shown by means of polarisation capacity measurements on passive iron that if there is a coating of oxide it must conduct electricity like a metal. He further points out that the assumption of the formation of a definite oxide is difficult to reconcile with the fact that on anodic polarisation a metal may take all intermediate potentials from the active to the passive condition. The latter objection is perhaps met to some extent by Haber's discovery that oxide films, in some cases at least, are porous, so that the mechanical hindrance to the escape of metallic ions would presumably increase with the thickness of the coating. A somewhat similar objection was advanced by Fredenhagen (*loc. cit.*), who applied a gradually increasing or a gradually diminishing e.m.f. to iron, nickel, or chromium electrodes immersed in sulphuric acid, and measured the p.d. at the electrodes and the strength of the polarising current. It was found that when the anode was slowly polarised the potential gradually became nobler, and then there was a rapid change to the passive condition. Conversely, when the electrode was allowed to recover its activity the potential fell gradually at first, and then there was a sudden transformation to the completely active condition. There was, however, no evidence of a definite activity or passivity potential, since the results depended on the concentration of the acid and other factors. These facts are very difficult to reconcile with the assumption that passivity is due to the formation of a definite oxide.

The most serious objection to the oxide-film theory, however, is based on measurements of the reflecting power of metallic surfaces. Müller and Koenigsberger (*Zeit. Elektrochem.*, 1907, xiii., 659) state that they are able to measure differences of 0·5 per cent in the reflecting power of two metallic surfaces, and in this way have detected the presence of oxide films of molecular dimensions (0·8 $\mu\mu$ in the case of lead peroxide). Two iron electrodes which had been polarised for some time by generating hydrogen and oxygen respectively in contact with them were found to show no difference whatever in reflecting power, although one was active and the other passive. The objection raised by Haber and Goldschmidt and by Krassa, that cathodic polarisation with rapid evolution of hydrogen had not reduced the oxide on the surface, and therefore that in both cases the reflecting power of oxidised films was being compared, does not seem very convincing.

The general impression gained by a review of the evidence is that although the oxide-film theory may apply in certain cases, especially to electrodes anodically polarised in alkaline solution, it can no longer be regarded as a satisfactory explanation of passivity in general.

The Valency Theory of Passivity.

This theory, first brought forward by Finkelstein (*loc. cit.*), is based on the assumption, due to Krüger (*loc. cit.*), that the modifications of a metal with different valencies are all present in the solid metal in proportions depending on the temperature and other factors, and that the electrochemical behaviour of metals depends on the relative concentrations of these modifications. W. J. Müller (*Zeit. Elektrochem.*, 1904, x., 832) has attempted to find support for this theory from considerations based on the electron theory of conductivity in metals. Both Krüger and Finkelstein recognise, however, that this theory affords no satisfactory explanation of *sudden* changes from the passive to the active condition, nor of the marked effect of the nature of the anion on passivity phenomena. The main point of the valency theory is that the cause of passivity is to be sought in the metals themselves, an assumption which is incompatible with the specific effect of the anions just referred to. The valency theory has met with very little support during the last four or five years, and therefore need not be further considered here.

The Reaction Velocity Theory.

As already mentioned the reaction velocity theory of passivity was first put forward by Le Blanc. One way of stating this theory is that metals in the passive condition send their ions of lowest valency only very slowly into solution. Thus in the case of iron the change represented by the equation $Fe + 2F \rightarrow Fe^{\cdot\cdot}$ proceeds very slowly when the metal is in the passive condition. This is not to be interpreted in the sense that the actual taking up of electric charges is a slow process (on the contrary, purely ionic reactions are practically instantaneous), but it is assumed that the ionisation of the metal is associated with *chemical* changes, and when these changes are very slow, passivity phenomena occur (compare Foerster, *loc. cit.*, p. 23). In its general form the reaction velocity theory is little more than a statement of the facts, and attention is mainly directed to the exact nature of the chemical changes associated with the purely electrical changes.

As already mentioned, there are at least four hypotheses as regards the nature of these chemical changes: (*a*) The oxygen charge hypothesis; (*b*) the anion discharge hypothesis; (*c*) the hydrogen activation hypothesis; (*d*) the retarded ion hydration hypothesis.

The Oxygen Charge Hypothesis.—Two or three years after the appearance of Le Blanc's paper on the subject, Fredenhagen (*loc. cit.*) put forward the view that passivity is due to the accumulation of a charge of gaseous oxygen on the metal, the slow reaction being that between metal and oxygen. Sudden changes from the active to the passive condition and *vice versa*, which sometimes occur, are ascribed to the transition from a non-homogeneous state of polarisation into a continuous gas charge covering the electrode uniformly. Even in the latter condition the electrode is not completely inactive, as a slow reaction takes place between it and oxygen.

There is no doubt that the oxygen charge theory represents a considerable advance on the oxide-film theory, since (1) it accounts for the effect of rise of temperature in removing activity; (2) it is not inconsistent with the results of optical measurements, since gas charges do not alter the reflecting power of metallic surfaces; (3) it is also, as an irreversible reaction, compatible with Fredenhagen's observation (*ante*) that the curve of gradually increasing activity does not correspond with that of gradually increasing passivity.

There are, however, formidable objections to the oxygen charge theory, of which the following may be mentioned:—

1. It does not account for Hittorf's "experimentum crucis" on the passivity of chromium in hydriodic acid (see above).

2. Certain metals which can be rendered passive combine readily with oxygen under other circumstances, and no explanation is afforded of their assumed inactivity towards this gas when in the passive state.

3. It does not account for the fact recently established by Grave (*loc. cit.*), that iron becomes passive on heating in nitrogen.

4. It affords no explanation of the passivating effect of alkalis on iron.

For these reasons the oxygen charge theory cannot be regarded as affording a satisfactory explanation of passivity phenomena.

The hypothesis of primary anodic discharge, first put forward by O. Sackur (*Zeit. Elektrochem.*, 1908, xiv., 612), promises to play a considerable part in the future development of electrochemistry. It has been generally assumed that when a metal dissolves at the anode, the primary process consists in a passage of the metal into solution in the form of ions. Sackur put forward his hypothesis of primary anion discharge without much experimental proof; for some time it met with little acceptance. Recently, however, support has been lent to this hypothesis by the observation of Haber and Zawadzki (*Zeit. Phys. Chem.*, 1911, xviii., 228) that when solid compressed silver salts are electrolysed between electrodes of silver considerable polarisation occurs, and this polarisation is greatly increased by lowering the temperature. The probable explanation is that the transport of the current from solid electrolyte to anode is effected by the passage of negative electrons from anions to metal; the discharged anions then attack the silver anode, the latter change being greatly retarded by cooling. It is not improbable that the mechanism of current transport is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode, so that little or no polarisation occurs.

It is evident that the above considerations afford an explanation of passivity phenomena on the basis of the reaction velocity theory. Sackur's explanation is rather complicated. He assumes that every electrode contains a certain amount of dissolved hydrogen formed by interaction with $H^{\cdot}$ ions in the electrolyte; the hydrogen concentration corresponds to the equilibrium represented by the equation (for a bivalent metal)—$Me + 2H^{\cdot} \rightleftharpoons H_2 + Me^{\cdot\cdot}$. The discharged anion (oxygen, halogen, &c.) reacts with and removes the hydrogen. To re-establish equilibrium the above reaction then proceeds in the direction of the upper arrow, so that the anodic dissolution of metals is a chemical process. Passivity is brought about by a slow rate of reaction between the hydrogen and the discharged anion, so that the latter (oxygen, &c.) accumulates on the electrode. There is considerable resemblance as regards the final stage between this hypothesis and the gas charge hypothesis. Although the above hypothesis is very suggestive, it is in one respect self-contradictory, as has been pointed out by Auerbach (*Zeit. Elektrochem.*). It starts with the assumption that the metals do not primarily ionise, whereas the assumed interaction of the metal with hydrogen is just such an ionisation.

The hydrogen activation hypothesis, based on the assumption that the *pure* metal is passive and only becomes active under the influence of a catalyst, was put forward by Foerster (*loc. cit.*) on the basis of a very detailed investigation of the electromotive behaviour of iron. If the reaction velocity theory, that passivity is due to the slow rate of ionisation of the metal, is correct, then since the reaction $Fe + 2F \rightleftarrows Fe^{\cdot\cdot}$ is reversible, the converse process, the electrolytic precipitation of iron, will probably also be a retarded reaction, a deduction which is fully confirmed by experiment.

Foerster points out that the hydrogen activation theory is in agreement with the effect of cathodic polarisation and of acids in promoting activity, also with the behaviour of iron in air, under the influence of oxidising agents, in the presence of alkali, &c. He does not deny that oxide films may play a part in passivity phenomena in certain cases, but considers that the production of such films is a consequence rather than a cause of passivity. In the case of anodic polarisation of iron in alkali, for instance, the underlying cause of passivity is the absence or removal of hydrogen, and the deposition of an oxide follows on account of the inactive condition of the metal. The chief advantage of this theory over the oxide theory is that it is valid both for polarisation in acid and alkaline solution. It is pointed out that other substances than hydrogen may facilitate the reaction $Fe + 2F \rightarrow 2Fe$; for instance, the presence in solution of substances capable of taking up negative or giving up positive charges, such as the halogens or metallic ions of higher valency, *e.g.*, $Fe^{\cdot\cdot\cdot}$. It is well known that the dissolution of passive metals is greatly facilitated by the presence of such substances.

Strong support has been given to Foerster's hypothesis by E. Grave (E. Grave, (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), who, however, contends that the catalyst is not hydrogen, or an alloy of hydrogen with the metal, as Foerster assumes, but hydrogen ions. In favour of this view the following facts are adduced. Iron and nickel become active when heated in hydrogen, but become passive when strongly heated in air, nitrogen, or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionised hydrogen renders the metals active, and iodised nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with $H^{\cdot}$ ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it in contact with hydrogen ions, other parts of the metal are rendered active by diffusion. This explanation of passivity has also been shown to afford an explanation of the well-known periodic phenomena at electrodes of chromium and other metals which can be rendered passive (A. Adler, *Zeit. Phys. Chem.*, 1912, lxxx., 385).

Quite recently, Flade and Koch (*Zeit. Elektrochem.*, 1912, xviii., 335) have attempted to decide between the oxygen and hydrogen theories of passivity as follows:—If an active electrode is heated and means are taken to remove any hydrogen given off, the metal must become passive if the hydrogen theory is correct, and active if the oxygen theory is valid. Further, if passive iron is heated in a vessel containing a reducing gas which is neither hydrogen nor a compound containing hydrogen, the metal must remain passive if the hydrogen hypothesis applies, and must become active if the oxygen hypothesis is valid. It was found that an active iron electrode remained active on heating in a vacuum, which speaks in favour of the oxygen theory. On the other hand, iron which had become passive by standing in air remained passive when heated in carbon monoxide, which appears to be contrary to the oxygen theory. It was found, however, that heating in carbon monoxide also renders active iron passive, and the author maintains that the result of the second experiment is also compatible with the oxide theory. With reference to the first experiment, the possibility of an objection to the effect that the metal after heating in a vacuum may still contain traces of hydrogen is foreseen, but is not regarded as valid.

Le Blanc's Views.—As Le Blanc was the first to put forward the reaction velocity theory of passivity, his views on the later developments of the subject are naturally of interest. I cite them according to the latest edition of his "Lehrbuch der Elektrochemie" (fifth edition, p. 283). Foerster's suggestion that pure iron is the passive form and that it only becomes active in the presence of a catalyst is apparently not accepted. It is assumed that active iron sends out ions into the electrolyte, and that in the case of metals which tend to become passive these ions only combine very slowly with water, according to the

equation Ion + water $\rightleftarrows$ ion hydrate. On this account the concentration of free ions at the electrode becomes so great, and therefore the potential difference between electrode and solution becomes so considerable, that the discharge of anions or of oxygen begins. This hypothesis of passivity is based on the observation that even when the ion concentration at the electrode is sufficiently large, polarisation occurs both at anode and cathode in many cases where it was not previously suspected (Le Blanc, *Abhandlungen der Bunsen Gesellschaft*, No. 3, 1910). In order to explain these facts a difference between free and hydrated ions is postulated, and it is assumed that the hydration and dehydration of ions is under certain circumstances a relatively slow process. It should be mentioned that this assumption is due in the first instance to Foerster and Luther (Foerster, *loc. cit.*, p. 55), and was applied by Foerster to account for the retardation observed in the discharge of $Fe^{\cdot\cdot}$ ions at an iron kathode. It may further be added that although the view that ions are more or less hydrated has met with wide acceptance, there does not appear to be any independent evidence of the slow hydration which forms the basis of Le Blanc's theory of passivity.

Conclusion.

The more important phenomena of passivity have now been briefly discussed, and the chief theories which have been put forward to explain these phenomena have been described. The main object of this paper is to afford a résumé of the present position of the subject, and it would be out of place in opening the discussion to attempt any detailed comparison of the relative merits of the different theories. This can be more profitably attempted when the various contributions to the discussion are available.

In all probability it will eventually be found that no one theory will serve to account for all the phenomena of passivity. Thus both Le Blanc and Foerster, although in the main favouring other explanations, recognise that the formation of insoluble films on the electrodes plays a part in some cases of passivity. The hydrogen activation theory, which is perhaps most in favour at the moment, is undoubtedly valid to some extent, as the effect of nascent hydrogen in restoring the activity of passive metals is beyond dispute. (According to Hittorf and Grave *molecular* hydrogen does not restore the activity of passive metals.) Whether iron entirely free from hydrogen is necessarily passive, as Foerster and Schmidt assume, would, however, appear to be still open to discussion. In particular, the activating influence of the free halogens (*e.g.*, iodine in potassium iodide) is difficult to reconcile with this view, as it would appear that the metal in the absence of hydrogen is capable under these circumstances of sending charged ions freely into solution, which is contrary to the theory. On the other hand, it should not be difficult to devise a plausible explanation of the *sudden* changes from the active to the passive state and *vice versa* on the basis of the hydrogen activation theory, whereas these changes are difficult to reconcile with any of the other theories. It is not easy to understand, for instance, how such sudden changes could occur on the basis of the ion hydration hypothesis favoured by Le Blanc.

Decomposition of Decahydroquinoline into Optical Isomers.—Bruno Veneziani.—The structural formula of decahydroquinoline is analogous to that of decahydronaphthol, each substance possessing two central carbon atoms and being asymmetrical. Decahydroquinoline being strongly basic can readily be split up into the two optical isomers by adding the calculated quantity of *d*-bromocamphosulphonic acid and subjecting to fractional crystallisation. The bromocamphosulphonate of the *d*-isomer is much the less soluble in water. The rotatory powers are as follows:—*d*-Decahydroquinoline, $[\alpha]_D = +1{\cdot}28$; *l*-decahydroquinoline, $[\alpha]_D = -1{\cdot}02$.—*Atti della Reale Accad. dei Lincei*, 1913, xxii. [ii.], No. 4.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

(Concluded from p. 239).

Complex Compounds.—Perhaps the most important work in inorganic chemistry during the past year has been that of Werner in his development of inorganic stereoisomerism and optical isomerism, especially in the complex compounds of cobalt. In the *Annalen* (cccIxxxvi., 1) he gives a complete review of his work on the stereoisomerism of cobalt compounds, much of which has been published from time to time in the *Berichte*. A few points in this work may be noted. Diethylenediamine compounds having different radicles in the other two places within the co-ordinated group as $\left(\begin{matrix}A\\B\end{matrix}Co\ en_2\right).C$, give rise to what Werner calls ionisation-metamerism, and furnish three isomers, according as the negative ion is A, B, or C. In addition each of these isomers may exist in both *cis* and *trans* form, according as A and B (or B and C, or A and C) are on contiguous or opposite corners of the fundamental octahedron of the co-ordinated group. Thus there are six possible isomers, and in the case where A, B, and C represent NO_2, Cl, and SCN, all six have actually been prepared. Some considerable progress has been made toward the systematisation of the properties of these compounds. For example, *cis* compounds generally are more soluble than the *trans* isomers, as is true of organic compounds; the colour of a compound is far more influenced by an element or group within the co-ordinated radical than by one outside; the order in which different groups within the radical affect the colour is the following, the first named having least effect:—CN, CO; NO_2, *en*, NH_3, NCS; SO_3; OH_2, O.NO, O-Acyl, OH; Cl, Br, I. In various intramolecular reactions transformation of isomers often occurs, but the direct transformation of stereoisomers into each other is rare, and probably results only from the formation of intermediate products. Three types of these reactions in which rearrangement may take place are noticed:—One (Einlagerungsreaktion), in which NH_3 or H_2O enters the complex radical, forcing the ionisation of group or atom of the complex, as—

$$\left(\begin{matrix}SCN\\Br\end{matrix}Co\ en_2\right).Br + NH_3 = \left(\begin{matrix}SCN\\H_3N\end{matrix}Co\ en_2\right).Br_2;$$

one (Verdrängungsreaktion), where NH_3 or H_2O passes out of the complex an atom or group outside the radical taking its place, as—

$$\left(\begin{matrix}H_3N\\Cl\end{matrix}Co\ en_2\right).(NO_2)_2 = NH_3 + \left(\begin{matrix}O_2N\\Cl\end{matrix}Co\ en_2\right).NO_2;$$

and a third (Substitutionsreaktion), where one negative atom or group is replaced by another. Inasmuch as the ordinary conception of replacement of atoms or groups, according to which an atom passes out of the group and the substituting atom takes its place, is inadequate to account for the stereometric changes which occur, Werner suggests a new theory. Every atom or group in the second sphere of a complex salt, that is outside the co-ordinated group, is attracted by the central cobalt atom, which seeks to draw the outside atom into the co-ordinated group. The *direction* of this attraction will depend upon the constitution of the complex; at all events this attraction will be stronger in some directions than in others. This will determine in what position the atom (or group) will enter the complex. On its entrance, the cobalt atom having but six co-ordination valencies, some other atom (or group) must leave the complex, and it will be the one for which the cobalt atom has (under the circumstances) the least attraction, and it may or may not be the atom which previously occupied the place where the newly entering atom has entered. Re-arrangements are thus not anomalous, but are founded on the ordinary course of the

* *Journal of the American Chemical Society*, xxxv., No. 2.

reaction. Werner suggests that the same idea is applicable to organic chemistry, where such transformations are by no means infrequent, and in particular calls attention to its applicability to the Walden re-arrangement.

One other class of products must be noted, which are formed by direct addition to groups within the co-ordinated complex. Such, for example, is the addition of a silver atom to the isothiocyanate group :—

$$\left(\begin{matrix}SCN\\H_3N\end{matrix}Co\ en_2\right).S_2O_6+AgNO_3=\left(\begin{matrix}AgSCN\\H_3N\end{matrix}Co\ en_2\right)\cdot\begin{matrix}NO_3\\S_2O_6\end{matrix}.$$

In such cases frequently the silver atom is not removed on treatment with HCl. This type of reaction is also exemplified by Kirmreuther's sulphaminic acid derivatives of the chloroplatinites described last year.

Werner has also developed the work begun the previous year on the optical isomerism of the cobalt complex (*Ber.*, xliv., 3272, 3279; xlv., 121, 3281, 3287, 3294). Numerous compounds of the types $\left(\begin{matrix}A\\B\end{matrix}Co\ en_2\right)$ and $\left(\begin{matrix}A\\A\end{matrix}Co\ en_2\right)$ have been prepared, and the racemic form split into the optical isomers, most frequently by the use of the bromocamphorsulphonates. In many cases it is possible to go from one compound to another without changing the character of the activity. The phenomenon of mutarotation sometimes appears; the chloronitro-compound increases from a rotation of $[\alpha]_D = 20°$ to a final constant of 52°. In other cases, as with the chlorobromo-compounds, the rotation decreases rapidly, and within an hour all activity has disappeared. Complexes were also prepared in which A and B in the above formulæ are represented by a single bivalent group, as carbonate and oxalate. The two compounds showed an opposite activity from that of the dichloro compounds from which they were derived, the lævo-dichloro-compound giving a dextro-carbonato- and dextro-oxalato salt. The carbonato salts have a high rotation, that of the chloride, $(CO_3Co\ en_2).Cl$ being $[\alpha]_D = \pm 350°$, while the carbonatodithionate is $[\alpha]_D = \pm 216°$, a much greater difference than is usual for different salts of the same complex. While the carbonato salts go slowly over into the racemic form the oxalato salts retain their activity even on boiling. Perhaps the most remarkable case of isomerism is that of the triethylenediamine compounds (Co en_3), where there are three identical bivalent groups in the complex, but which should exist in two non-superposable forms. Here the bromocamphorsulphonates gave no assistance in resolving the isomers, but by adding sufficient silver tartrate to precipitate two of the three atoms of chlorine in (Co en_3).Cl_3, the dextrochlorotartrate crystallised out, and the lævo salt formed was recoverable from the mother-liquor. From these salts both forms of optically active chlorides, bromides, and nitrates were formed. The corresponding triethylenediamine chromium racemates could not be resolved by tartrates nor by bromocamphorsulphonates, but by using nitrocamphor this was accomplished (*Ber.*, xlv., 865). The rotation of the optical isomers of these chromium salts was less than that of the cobalt salts, confirming what had already been found regarding the dichloro-diethylenediamine salts of these two metals. A further development of this work on inorganic optical isomerism is the preparation by Werner (*Ibid.*, p. 1228) of the optical isomers of triethylenediamine rhodium salts. Here the racemates could be split both by the tartrate and the nitrocamphor method, and the isomers showed decided stability, it being possible to evaporate the solutions without decreasing their optical activity. How much the nature of this activity depends upon the special nature of the central atom is shown by the fact that while the rotation of the rhodium compounds is quite similar in amount to that of the corresponding chromium compounds, it is opposite in sign, those rhodium salts having the same composition and configuration as the dextro-chromium salts, being lævorotary. Werner was also able to prepare (*Ibid.*, p. 433) by the tartrate method the lævorotatory form of tri-*aa*-dipyridyl iron chloride, bromide, and iodide. The rotation is very high (in the neighbourhood of 500°), but falls rapidly owing to formation of the racemate. It thus appears that inorganic optical isomerism is not confined to ethylenediamine compounds, nor to the eompounds of trivalent metals, since the iron in the pyridyl eompound is bivalent. It should, however, be noted that in spite of the most brilliant confirmation of Werner's theories by his work of the last two years, the whole co-ordination theory is quite severely handled by Stewart in his "Recent Advances in Physical and Inorganic Chemistry" (1912, p. 160).

In this connection attention may be called to the work of Costachescu (*Ann. Scient. Univ. Jassy*, vii., 87, 132), who by action of pyridine on ferrous chloride obtains $(FePy_4)Cl_2$. Evaporated with HCl there is formed $(Fe_2.3PyHCl)Cl_6$, or with HBr, $(Fe_2.3PyHBr)Cl_2Br$. With $(Cr(H_2O)_6)F_3$ pyridine gives $\left(Cr\begin{matrix}Py_3\\F_3\end{matrix}\right)$, and by elimination of one pyridine, the aquofluoride, $\left(Cr\begin{matrix}Py_2\\F_3\\H_2O\end{matrix}\right)$. The conductivity of both these compounds is zero, as would theoretically be expected, and neither chromium nor fluorine is precipitable. By the further action of pyridine there were formed salts of the univalent radical $\left(Cr\begin{matrix}Py_4\\Fe_2\end{matrix}\right)$, which acted like a univalent metal.

A study of the equilibrium between purpureo- and roseo-cobalt chlorides,—

$$\left(Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right)Cl_2+H_2O\rightleftharpoons\left(Co\begin{matrix}H_2O\\(NH_3)_5\end{matrix}\right)Cl_3,$$

by Lamb and Marden (*Journ. Am. Chem. Soc.*, xxxiii., 1873) shows that this is a monomolecular reaction, and apparently consists in the slow ionisation of the chlorine atom of the purpureo-complex, a water molecule taking its place. By analogy the same thing would be expected in the dissociation of an ordinary electrolyte. In the dry state the roseo-salts have a critical vapour pressure above which only a very slow loss of water occurs, but the change does not appear to be reversible.

A method of investigating residual valence for ammonia in ammoniates is given by Peters (*Zeit. Anorg. Chem.*, lxxvii., 137), which consists in subjecting the dry salt to the action of a measured amount of ammonia in a eudiometer, driving off the ammonia by a vacuum, and then re-saturating it. The results with nearly a hundred salts are tabulated, and the compounds are, in general, what would be expected from Werner's theory, the number of ammonia molecules taken up being most frequently six or a multiple of six. In some cases the ammonia was evidently taken up by both cation and anion, but the distribution could not generally be determined. By this work an interesting line of study has been opened up. Inghilleri (*Atti Accad. Fisiocrit. Siena*, 1909, p. 6) has prepared by the action of quinoline on uranyl salts, a series of complex salts of the general type, $[(C_9H_7N)_2UrO_2]X_2$, including the nitrate, sulphate, acetate, oxalate, and tartrate, as well as double salts. By using aniline in the place of quinoline (*Ibid.*, 1911, p. 3), the sulphate, acetate, and oxalate of the base, $[(C_6H_5NH)_2UrO_2]$, were obtained, as well as the compound, $C_6H_5N.UrO_2.6H_2O$. In connection with complex salts mention should also be made of the continuation of Weinland's work on the chromi-acetates (*Zeit. Anorg. Chem.*, lxxv., 293), where the complex cation contains three chromium atoms with six or less acetate groups, and OH, H_2O, or NH_3. More than a score of different types are described, though they seem as yet not capable of systematisation. In studying the ammoniates of cuprous-mercuric iodides, Anderlini (*Gazz. Chim. Ital.*, [I.], xlii., 321) has prepared $CuHgI_3.2NH_3$, $CuHg_2I_5.3NH_3$, and $CuHg_2I_5.4NH_3$, all of which are rather unstable, and become red on standing in the air.

Ephraim (*Ber.*, xlv., 1322) has made use of the ammoniates in his studies of "Nebenvalenzen." While i$_t$

would be difficult to measure directly the force which holds molecular complexes together, it is possible to measure the energy which must be added to decompose them. The decomposition is dependent on pressure, temperature, and the affinity which holds them together. If the pressure is kept constant the temperature of decomposition is a direct function of the energy of formation. This, Ephraim has determined for a large series of ammoniates of the salts of bivalent metals, and finds that the decomposition temperature increases with the decrease in atomic volume of the central (metallic) atom; indeed, the product of the cube root of the decomposition temperature (absolute) by the atomic volume of the central atom is approximately constant. The vapour pressure of the ammoniates can thus be approximately calculated from the atomic volume. The atomic volume is naturally not the only factor which controls the stability of the ammoniates. Thus no metal whose atomic volume is greater than fourteen can form a hexa-ammoniate at ordinary temperature, and no atom except those of the alkaline earths can hold more than six ammonia groups; the octa-ammoniates of these earths must have a special interpretation. The negative atom or group has also something of a determining influence, and the relation between the difference in influence of different negative groups (as Cl-Br) is constant for different metals. Another class of complex saits which is being studied by Copaux (*Zeit. Anorg. Chem.*, lxxiv., 351) and Rosenheim (*Ibid.*, lxxv., 141; lxxvii., 232) as well as by Miolate, is the hetero-poly acids, containing WO_3 and MoO_3. Copaux draws a distinction between what he considers the normal and the secondary basicity of these acids, a distinction which Rosenheim deems unnecessary, and which would, if logically carried out, demand that we should consider phosphoric acid normally dibasic and secondarily tribasic. The free dodeka acids are represented by $H_7[P(W_2O_7)_6].28H_2O$, $H_8[Si(W_2O_7)_6].28H_2O$, and $H_9[B(W_2O_7)_6].28H_2O$, which are isomorphous; the two former of these are metastable at ordinary temperature, and lose water passing into the 22-hydrate. Isomorphous molybdo-phosphoric and molybdo-silicic acids exist, the former also as a 22-hydrate. The 22-hydrates are also isomorphous with each other. The only hydrate of metatungstic acid which Rosenheim could prepare was the 12-tungsto-aquo acid, $H_{10}[H_2(W_2O_7)_6].22H_2O$, though he considers the 28-hydrate probably capable of existence. This metatungstic acid is also isomorphous with the other 22-hydrates. Prandtl has begun (*Ibid.*, lxxiii., 223) the systematisation of the poly acids containing vanadic acid, which seem to be derived from a hexa-vanadic acid, $H_4V_6O_{17}$, whose salts can be made. The seleno-vanadates are derived from this acid with the addition of $4SeO_2$, or in some cases $4H_2SeO_3$, and also with a larger number of SeO_2 molecules, probably with 5, 6, 8, 10, and 12 SeO_2. The NH_4 and K salts of the last, dodeka-selenite, were obtained, and this seems to be the limiting compound. The tungsto- and molybdo-vanadates seem also to be derivatives of the same hexa-vanadic acid.

Finally, under the head of complex compounds mention must be made of further development of the work of Tschugajew (*Comptes Rendus*, cliv., 33) on the platinum bases containing organic sulphides, and of Fritzmann (*Zeit. Anorg. Chem.*, lxxiii., 239) on analogous selenium compounds. The addition of dithioglycoldiethylether to potassium bromo-platinite gives a grey salt, $[Pt.2(C_2H_5.S.CH_2.CH_2.S.C_2H_5)].PtBr_4$, a salt of the type of Magnus's salt. On warming this goes over into the monomeric form, $Pt(C_2H_5.S.CH_2.CH_2.S.C_2H_5).Br_2$. Since the sulphide is bivalent, only the *cis*-form is possible, and no isomer of the monomeric form was found. With methyl (and other) selenides, three isomers (with chloro-platinite) were found, the *cis*- and the *trans*-forms, $(CH_3)_2Se \rightarrow Pt \leftarrow Cl$ ($(CH_3)_2Se$ and Cl) and $(CH_3)_2Se \rightarrow Pt \leftarrow Cl$ (Cl and $Se(CH_3)_2$), and also the dimeric form corresponding to Magnus's salt, $[Pt((CH_3)_2Se)_4].PtCl_4$. With diethyltrimethylene diselenide only two isomers were formed, since here, where there are two selenium atoms in the same group, no *trans*-form is possible. This corresponds to the case with ethylenediamine. Many other papers on complex compounds must be passed over, but it is evident that this is to-day the most active field of investigation in inorganic chemistry. In the past, while many of these compounds were known, chemists had to pass them over with possibly an empiric formula. To-day, armed with all the modern refinements of research the chemist is beginning to bring order out of chaos.

In conclusion, it may be noted that nothing further has been heard regarding canadium, the new metal of the platinum group, supposed to have been found in British Columbia. Nor have the efforts to confirm the results of Flint in splitting tellurium by hydrolysis had any positive outcome.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Longevity of Microbes.

The numerous experiments of M. Trillat and of his pupils had already shown the influence of the presence of gaseous emanations in the air on the longevity of microbes. It is thus that M. Trillat has recognised that the impurities that are daily diffused in the atmosphere, and which proceed from the decomposition of organic matters of animal or vegetable origin, form an extremely favourable environment for the longevity of certain infinitely small microbes. Newly exhaled breath, the emanations of the earth, the neighbourhood of bodies in a state of decomposition, are all sources of gaseous aliments for microbes. The experiments made by M. Trillat on the air of glaciers and air taken in the neighbourhood of habitations have clearly demonstrated this influence. M. Trillat, in collaboration with M. Fouassier, has continued this study which has been presented to the Academy of Sciences by M. Laveran. The two scholars have just shown that the transport of pathogenous microbes in the air is effected especially by the damp which contains, in an infinitesimal state, traces of gas-aliments. Moreover, it would seem that the air when it fulfils certain conditions of dampness, of chemical composition, of temperature, and of age of microbes, is capable of being fertilised directly by the contact of a microbian source. Up till now it was thought, according to numerous observations of the German scholar Flugge, that for microbes to be transported by the air it was necessary to project them into it by some mechanical action, such as pulverisation or any other means, the effect of which would be to detach them from their support. Contrary to this notion, MM. Trillat and Fouassier have established experiments demonstrating that when the superposition of certain factors takes place, the sowing of the air is performed in the same manner as that of a bouillon of culture, merely by the play and movement of the invisible vesicles which constitute the humidity of the air. In an infinitely feeble volume of about one hundred thousandth of a cubic millimetre these tiny drops are uninfluenced by the action of the force of gravity. They are always mobile under the influence of the least variation of temperature. All these results are of the greatest interest for bacteriological science. MM. Trillat and Fouassier have shown how the contamination of the air takes place in a closed and tranquil space, without the intervention of the presence of dust or of any mechanical means, as was believed up to the present time.

The Multiplication of Oysters.

A naturalist of the Natural History Museum, M. Dantan, has shown that the greater number of breeding oysters can breed and produce from their first year. An oyster of twelve or thirteen months old, measuring about 34 mm.,

produces about one hundred thousand larvæ. Oysters of two years of age contain on an average two hundred and fifty thousand, and one of three years of age seven hundred and twenty-five thousand larvæ. In a paper presented to the Academy of Sciences by M. Edmond Perrier, director of the Museum, M. Danton indicates that in oysters of one year the proportion of individuals that give birth to female oysters is very weak. It is only during the third year that oysters approach the normal state of breeding. On the French oyster-beds, where the growth is in the beginning very slow, the reproduction does not begin from the first year. As that appears to be the case of protandric hermaphrodism, while the oyster is laying the greatest number of eggs it is the male sex that predominates.

The Geological Rôle of Fluorine.

A very important communication has been made to the Academy of Sciences by Prof. Armand Gautier on the presence of fluorine in the igneous reactions of the nucleus of the globe. The work of the eminent chemist explains a geological fact misunderstood up till now—the existence of fluorine in all grounds of which it characterises the direct or indirect igneous origin; in the virgin thermal springs, which are formed in the bosom of the igneous rocks, and in the eruptive or volcanic gases in which it had not before been observed. At the present time, M. Armand Gautier has been able to establish the fact that fluorine forms a part of all old rocks, that it always remains in the state of fluorite, apatite, &c., as well as in the waters that flow out of these veins. From all times fluorine has thus come out of the terrestrial nucleus, and it still continues to be produced. But up till now it had been impossible to realise this research in the eruptive gases for want of a method. M. Armand Gautier has succeeded in finding one and also in estimating it. In the month of August last, at an altitude of 1080 metres, at the mouth of the volcano of Vesuvius, he managed to collect the gas of the fumaroles. In it he noticed some fluorhydric acid. He also collected, not far from Voltera, in the Tuscany beds of boracic acid, gases issuing from the soil at 160°, and likewise containing free fluorhydric acid. The condensed water that accompanies these gases contains 3·72 mgrms. of fluorine. So then, whether we examine the old rocks, granites, or porphyries, the soils that proceed from them, the mineral waters that flow from them, or the eruptive gases, always and everywhere fluorine is present and characterises the igneous origin of these products. Fluorine, concludes Prof. Armand Gautier, for want of the means of following it up, has remained up till now the great misunderstood geological and physiological actor.

The Temperature of Arc Lamps.

M. Lummer has just concluded a series of experiments to see if really carbon boils like water; that is to say, if the temperature of ebullition increases when the pressure augments. According to M. Violle, the temperature of the electric arc, in the crater, is the temperature of the volatilisation of carbon. The temperature of the crater of the positive carbon may be estimated at 4000°, that of the negative being from 600° to 700° lower. If the temperature depends upon the pressure it would be possible by increasing this latter to augment the temperature of the arc far beyond the present temperatures. The quantity of light produced would also be greater. The experiments undertaken by M. Lummer seem to prove that it will be possible to arrive at a greater luminous intensity.

Salt Increases the Fertility of the Soil.

Sea-salt seems to play a rather important *rôle* in the development of plants. M. Armand Gautier explains its fertilising properties by the fact that chloride of sodium favours the solubilisation of potassic felspars. M. André, in whose name the paper on the subject is presented to the Academy, adds that carbonate of calcium and sulphate of ammonium do the same. They favour the dissolution in water of the felspars, and of potassic salts, which constitute the mineral aliment of plants.

Radium and Plants.

Recent experiments made in Bohemia and France have led learned men to think that this precious metal, which in a pure state is worth from 700,000 to 800,000 francs per grm., might renovate methods of cultivation. The radioactive properties mixed with the manure seems to serve as a stimulant and to push on the vegetation, giving it at the same time a greater vigour. A great number of experiments made, as well for market-gardening as for the cultivation of wheat, corn, and beet-root, have shown this marvellous action of radium on plants. Other experiments, consisting in the judicious use of radio-active manures in the cultivation of the vine, have had the effect of protecting the vineyards against cryptogamic diseases. Lastly, quite lately, in a paper presented to the Academy of Sciences by M. Maquenne, Professor at the Natural History Museum, M. Stocklasa, of the University of Prague, announces that, according to his personal researches, the radiation and emanation of radium exercise a favourable action on a certain number of microbian species that are of interest to agriculture, especially those that directly fix the nitrogen of the air and those that transform the complex nitrogenised matters into ammonia. It would then seem that the emanation of radium contributes to the increase of the natural fertility of the soil by augmenting its richness in assimilable nitrogen.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 5th, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. Charles William Birch, Ulick Richardson Evans, and Harold Warren Gill were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Alan Milsom Bailey, Lanhill, Chippenham, Wilts; Arthur Leslie Barton, 80, Hotham Road, Putney Common, S.W.; Thomas Sidney Haines, 24, Woodfield Avenue, Ealing; and Arthur George Abraham Miller, 1, Pretoria Terrace, Waltham Cross, Herts.

Certificates were read for the second time in favour of Messrs. John Joseph Eastick and J. F. Millar.

The following papers were read and discussed:—

"*Preparation of Rubber for Analysis.*" By L. Archbutt.

The author exhibited a machine for grinding rubber samples and gave some results showing the effect of grinding upon the analytical figures obtained in the analysis of rubber.

Other matters of interest in connection with rubber analysis were also discussed.

"*Examination of Commercial Gelatins in reference to their Suitability for Paper-making.*" By R. W. Sindall and W. Bacon.

Various analytical details of the chemical constituents together with the determination of viscosity and tenacity were dealt with, and more particularly the relation of such physical factors to the actual sizing operations as carried out in the mill.

"*Properties of some Chlorhydrocarbons and their Uses in Chemical Analysis.*" (Part I.). By L. Gowing-Scopes.

The author gives the latest figures for the physical pro-

perties of the chlorethanes and chlorethylenes compared with those of chloroform and carbon tetrachloride. The solubilities of 245 substances, and the action on common metals and inorganic compounds are also given. Their use for fat extractions and their uses in analyses are included, together with a discussion of their chemical properties.

"*Detection and Estimation of Benzoic Acid in Milk and Cream.*" By E. Hinks.

Milk or cream is heated with an equal volume of hydrochloric acid till proteids are dissolved. The fat and benzoic acid are extracted with ether and petroleum ether; the benzoic taken back into ammoniacal water. This solution is tested qualitatively for benzoate, while the benzoic acid may be recovered quantitatively by acidifying, extracting with ether, evaporating spontaneously, and finally subliming in steam oven. The loss on heating gives the benzoic acid.

NOTICES OF BOOKS.

The Cyanide Process of Gold Extraction. By James Park. Fifth English Edition. London: Charles Griffin and Co., Ltd. 1913.

This book belongs to the series of authorised text-books of the Australian Schools of Mines, and is one of the best books on the subject extant. Both the metallurgical process of cyanide extraction and the necessary laboratory control work are fully described in it, and many papers of importance which have appeared in periodical literature or have been read before meetings of scientific societies are reprinted or summarised. For the fifth edition the text has been very carefully revised, and some recent notable advances, such as the process of vacuum filtration, are discussed.

A Text-book of Assaying. By C. and J. J. Beringer. Revised by J. J. Beringer. Thirteenth Edition. London: Charles Griffin and Co., Ltd. 1913.

This text-book on assaying for the use of students of schools of mines and assayers contains full working directions for all the usual methods of assaying, both gravimetric and volumetric, and an excellent course of practical work could readily be based upon it. In the thirteenth edition the assay of wolfram is treated more fully than before, and the sections on the wet assay of tin ores have also been partly re-written.

New Standard Dictionary. London: Funk and Wagnalls, Salisbury Square, Fleet Street, E.C.

This important work produced by Messrs. Funk and Wagnalls, of which we gave a short preliminary notice a few months ago, has now been published, and the two handsome volumes contain a large amount of valuable information resulting from an unusual expenditure of highly skilled labour.

Among the names of the contributors are seen those of Lord Avebury, Sir James Crichton-Browne, Sir Hiram Maxim, Earl Roberts, and many other notable men.

The publishers deserve great credit for their bold originality in the arrangement of the work. They have succeeded in placing the maximum amount of information in such a position that it can be consulted with a minimum expenditure of trouble. Much thought has been given to the important subject of pronunciation, and the definitions given are the outcome of the decisions of a committee of leading experts. In the matter of quotations, which are both lengthy and numerous, the authors' names are always given.

It is the intention of the publishers to combine the advantages of a dictionary and an encyclopædia, and they have largely succeeded in their aim; the two volumes are not too cumbersome to have close at hand, and they will in many cases render the reference to larger works unnecessary.

Cyanamid: Manufacture, Chemistry, and Uses. By Edward J. Pranke, B.Sc. Easton, Pa.: The Chemical Publishing Company. London: Williams and Norgate. 1913.

The author of this monograph has endeavoured to give his readers an unbiased account of the properties and uses of cyanamide, which he believes will play a very important part in the future development of scientific agriculture. Without doubt enough work has been done on the properties and action of this fertiliser to warrant our regarding it as in most respects raised out of the sphere of controversy, although, on the other hand, there is need of further research on some still-disputed questions of detail, and the monograph will serve a double purpose—to give the intending user of the substance a knowledge of its properties and application, and to suggest fresh lines of investigation to the chemist. The decomposition of cyanamide in the soil, and in particular the work of Ulpiani and Kappen, is critically discussed and well summarised, and the question of its toxicity is also treated in an unprejudiced spirit.

Einführung in die Thermodynamik. ("Introduction to Thermodynamics"). By R. Blondlot. Translated by Carl Schorr and Friedrich Platschek. Dresden and Leipzig: Theodor Steinkopff. 1913.

A book which has been translated at the suggestion of Prof. Ostwald can be sure of a good reception in Germany, and the authorised translation of the second French edition of this work will undoubtedly be widely used. Both as regards the material and its presentation and arrangement it is unexceptionable, and for those who are beginning the study of thermodynamics it can be confidently recommended. It contains a complete exposition of the Principle of Equivalence, and Carnot's Principle, giving details of experimental proofs, and explaining their mathematical expression and their application to some natural phenomena. In the last chapter energy is defined and discussed, and the physical significance of the principle of the conservation of energy is explained.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 2, 1913.

Action of Halogens on Artemisine.—E. Rimini and T. Jona.—Bromine and iodine react with artemisine in exactly the same way as with santonine, if the reaction takes place in presence of the hydracid. Two molecules of artemisine give rise to products in which two atoms of halogen are present in the active state and one in the hydracid form. These substances, the empirical formulæ of which are $C_{30}H_{37}O_8Br_3$ and $C_{30}H_{37}O_8I_3$ respectively, are very unstable, and regenerate artemisine in presence of cold water. With chlorine artemisine reacts differently, a dichlorate of formula $C_{15}H_{20}O_4Cl_2$ being obtained.

Researches on Hydrazones.—L. Vecchiotti.—R. Ciusa has shown that nitrohydrazones can exist in different chromoisomeric modifications. The red form has the malenoid and the yellow the fumaroid structure, and it is obvious that in some cases, *e.g.*, the phenylhydrazine of *o*-nitrobenzaldehyde, the red form will be the more stable. The formation of a pentatomic ring hinders the passage of the malenoid into the fumaroid form.

Vol. xxii., [ii.], No. 3, 1913.

Formula of Chlorhydrate of Apomorphine.—V. Paolini.—Determinations of the water of crystallisation of various specimens of the chlorhydrate of apomorphine obtained from different sources have given as the percentage of water present 4·2, *i.e.*, that calculated from the

formula $C_{17}H_{17}O_2N.HCl + \frac{3}{2}H_2O$. If the chlorine is estimated volumetrically in the anhydrous residue it is found that the formula of the chlorhydrate is undoubtedly $C_{17}H_{17}O_2N.HCl$, and Dott's formula containing C_{34} is not correct. The depression of the freezing-point of the dibenzoyl ether indicates that the formula of apomorphine is the simple formula $C_{17}H_{17}O_2N$.

New Derivatives of Axoxybenzene.—Bruno Valori.—Zinin's *p*-nitroazoxybenzene gives with nitric acid *p*-dinitroazoxybenzene. while with bromine a 2-nitro-4-bromo derivative is obtained. A dibromo derivative can be prepared by allowing bromine to act upon this substance in a closed tube in presence of a catalyst, such as iron filings. Concentrated sulphuric acid with dibromoazoxybenzene gives dibromoazobenzene, from which the original dibromoazoxy compound can be regenerated by oxidation with hydrogen peroxide in acetic solution. Tribromoazobenzene can be obtained by the action of bromine on dibromoazobenzene.

MISCELLANEOUS.

Institute of Chemistry.—Mr. W. P. Dreaper, F.I.C., will deliver the Second Lecture on "The Research Chemist in the Works, with special reference to the Textile Industry," on Wednesday, November 26th, at 8 p.m., at the Imperial College of Science and Technology, South Kensington, W.; Prof. Raphael Meldola, D.Sc., F.R.S., President, in the Chair.

Lawes and Gilbert Centenary Fund.—It is proposed to erect at Rothamsted a Commemoration Laboratory to celebrate the centenary of the birth of Sir John Lawes in 1814 and of Sir Henry Gilbert in 1817. A sum of £12,000 is required for the purpose, but it is understood that if one-half of this amount can be raised by subscription, the other half will be forthcoming in the form of a grant. An appeal is therefore being issued for the sum of £6000. Subscriptions should be sent to the Secretary, The Rothamsted Experimental Station, Harpenden, cheques being crossed Robarts, Lubbock, and Co.

New Catalogue.—Messrs. A. Gallenkamp and Co., Ltd., of 19—21, Sun Street, Finsbury Square, E.C., have sent a copy of their new catalogue, containing amongst other pieces of apparatus, many recent forms of calorimeters, CO_2 recorders, Haldane's apparatus for the analysis of air in workshops and mine gases, &c. Much space is also given to the various forms of pyrometers that have recently been introduced, particularly the beautiful instruments devised by Prof. Féry. The firm is to be commended for their enterprise in fully illustrating and describing the many novel devices that have recently been placed at the service of chemical and physical science.

MEETINGS FOR THE WEEK.

WEDNESDAY, 26th.—Royal Society of Arts, 8. "Zoological Gardens," by P. Chalmers Mitchell, D.Sc., F.R.S.

THURSDAY, 27th.—Royal Society. "Method of Measuring the Pressure produced in the Detonation of High Explosives or by the Impact of Bullets," by B. Hopkinson. "Gravitation Instability and the Nebular Hypothesis," by J. H. Jeans. "Diffraction of Light by Particles Comparable with the Wave-length," by B. A. Keen and A. W. Porter. "The Colour of Zircons, and its Radio-active Origin," by R. J. Strutt. "Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-Ray Spectrometer," by W. H. Bragg. "Analysis of Crystals by the X-Ray Spectrometer," by W. L. Bragg.

—— Chadwick Public Lectures, 5. (Hartley University College, Southampton). "Military Hygiene, the History of Physical Efficiency in the Army," by Surgeon-Gen. G. J. H. Evatt, C.B.

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THE CHEMICAL NEWS

VOL. CVIII., No. 2818.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

THERE used to be a general tendency to assume that both the formation of metallic ions in the anodic dissolution of a metal and the transition from the ionic into the metallic state in cathodic deposition were processes which took place at a practically infinite velocity. On that view a metallic anode, immersed in a solution of one of its salts, should with anodic polarisation pass into solution as soon as the equilibrium potential was slightly exceeded which the respective electrode possessed in that solution. Some rise in the potential above the equilibrium value, and thus some polarisation, was to be expected only in so far as it would be demanded, according to the formula of Nernst, by an increase in the concentration in the immediate neighbourhood of the anode. In cases where a higher polarisation was noticed, such that potentials were attained which permitted of an evolution of oxygen simultaneous with the dissolution of the metal, or merely of an evolution of oxygen unaccompanied by a formation of metallic ions, the cause of this "passivity" was frequently ascribed, with Faraday, to the formation of a film of oxide on the electrode. It was the great merit of M. Le Blanc to have pointed out that, with certain metals, the passivity finds its explanation in the circumstance that these metals emit their ions of lowest valency into the solution at a greatly restricted velocity (*Zeit. Electrochem.*, 1900, vi., 472; "Lehrbüch der Elektrochemie," 1903, 3rd edition, p. 237).

Since now it is a fact that, in the case of one and the same metal which can be rendered passive, the formation of cations takes place at a much more rapid rate when it is in the active state than when in the passive state, we have to ask ourselves how these great variations in the velocity of reaction can arise. There were two possible explanations: either we suppose the rate of formation of ions in the active state to be characteristic of the metal—in that case the retardation of the velocity of reaction in the passive state had to be attributed to the effect of a negative retarding catalyst; or we assume the passive state of metals (which can be passivated) to be the normal state—in that case the marked acceleration in the formation of the ions in the active state could only be due to the effect of some accelerating catalyst. Both these possibilities have been taken into consideration. W. Muthmann and Fraunberger (*Sitzber. Bayer. Akad. Wissensch.*, 1907, xxxiv., 201), as well as Fredenhagen (*Zeit. Physik. Chem.*, 1903, xliii., 1; *Zeit. Elektrochem.*, 1905, xi., 857; *Zeit. Physik. Chem.*, 1908, lxiii., 1) suggested that a solid solution of oxygen is formed on the surface of the metal (which can be rendered passive) when it is anodically polarised or treated with oxidising agents, and that this fact causes the retardation in the emission of ions. F. Foerster (*Abhandlungen Bunsen-Ges.*, 1909, No. 2), on the other hand, advocated that the passive state was normal for certain metals, and that the accelerated formation of cations from these metals in the active state was due to the hydrogen adsorbed by the metallic surface. Foerster was led to this view by the observation, which he and others had frequently made, that whenever iron become active, hydrogen was liberated at it. It was further known that iron, from which hydrogen had once been evolved, could take up small quantities of hydrogen, and would thereby change its properties in the sense that it became highly reactive chemically. The potential of an iron electrode, cathodically polarised with hydrogen, against normal ferrous sulphate also shows less noble values than would correspond to the equilibrium of pure iron with regard to that solution (*Abhandlungen Bunsen-Ges.*, 1909, No. 2, p. 9). The hypothesis hence appears plausible that it is hydrogen which catalytically accelerates the emission of ions from the iron. It will be understood that, like Le Blanc, Foerster finds the cause of the passive state in a diminution of the rate of cation formation. It is a consequence of the strongly retarded formation of ions from metals which can be passivated, that these metals, when anodically polarised, easily assume potentials which correspond to a weak charge of the electrode with oxygen. This oxygen, which in the first instance is a consequence of the passivity, will in its turn be able to impede still more the in itself retarded process of ion-formation at the anode, and will thus lead to a further rise of the anode potential; this potential will finally attain values such that oxygen liberation sets in at the anode in addition to the formation of metallic ions, and that this oxygen liberation may claim the main share of the polarisating current. A complete cessation of the formation of metallic ions owing to the impeding action of the oxygen charge is, however, rare. There will thus be a possibility that the cations emitted from the anode at small rate will combine with the oxygen taken up by the anode surface to oxidic precipitates which, like the oxygen charge, must be regarded as a secondary consequence of the passive properties of the anode metal, not as their cause.

That the fundamental view of the theory of passivity of Le Blanc as just outlined is correct, that is to say, that both anodic dissolution of a metal and cathodic deposition of a metal may be retarded phenomenona, has within recent years been established by many experimental researches (*cf. e.g.*, M. Le Blanc and M. G. Levi, *Annal. d. Physik.* (Boltzmann Festschrift), 1904, p. 183; F. Foerster, *Abhandl. Bunsen-Ges.*, 1909, No. 2; M. Le Blanc, *Ibid.*, 1909, No. 3; A. Schweitzer, *Zeit. Elektrochem.*, 1909, xv., 602; R. Schildbach, *Ibid.*, 1910, xvi., 967; H. G. Byers, *Journ. Am. Chem. Soc.*, 1908, xxx., 1718; E. P. Schoch, *Trans. Am. Electrochem. Soc.*, 1908, xiv., 99; E. P. Schoch and C. P. Randolph, *Journ. Phys. Chem.*, 1910, xiv., 719, &c.).

It would lead us too far to discuss the results of all these researches. I will content myself with dealing with the second part of Foerster's passivity theory, according to which the small velocity of reaction marking the anodic dissolution and the cathodic deposition of passive metals does not alone suffice to focus the whole domain of activation and passivation, and that we are hence forced to assume a co-operation of positive and negative catalysts on the electrode. The following important question thus suggests itself as concerning the problem of passivity: In how far is the velocity of reaction, and hence the variation of the potential in anodic and cathodic processes, influenced catalytically by the occurrence of small quantities of foreign substances on the surface of the electrode?

I should like now to place before you some experimental researches which F. Foerster and his pupils have undertaken within the past few years in order to answer that question. In the first instance I propose to dwell upon the retardation observed in the emission and deposition of metallic cations; I shall afterwards touch upon the retardation phenomena which occur in the discharge of anions.

Le Blanc (*Abhandl. Bunsen-Ges.*, 1909, No. 3) on the one hand, and F. Foerster and his pupils on the other (*Ibid.*, 1909, No. 2; A. Schweitzer, *Zeit. Elektrochem.*, 1909, xv., 602; R. Schildbach, *Ibid.*, 1910, xvi., 967), had found that the cathodic deposition of the metals of the iron group takes place at a diminished rate, This process now, as F. Foerster has demonstrated in conjunction with

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12, 1913.

W. Treadwell, jun., and W. von Escher, may undergo a further retardation when there are also present small quantities of zinc on the surface of the cathodically deposited iron-metal.

The experiments of W. Treadwell ("Dissertation," Zürich, 1909: *cp.* also F. Foerster, *Zeit. Elektrochem.*, 1911, xvii., 883) were undertaken in order to inquire into is in excess, yield a deposit in which zinc predominates; this is so at all the current densities at which any metallic deposits can be secured. The cathode potential assumes during the electrolysis values which come up very close to those of a pure solution of zinc sulphate at corresponding current densities. Fig. 1 exemplifies the results of a series of experiments conducted at 18° with a solution which was

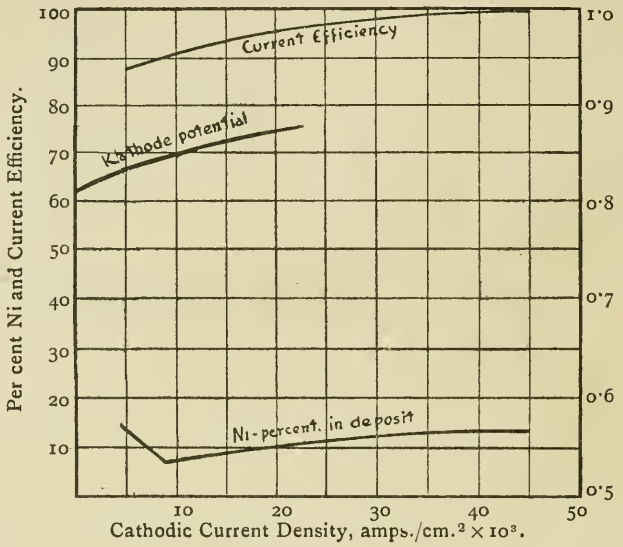


FIG. 1.

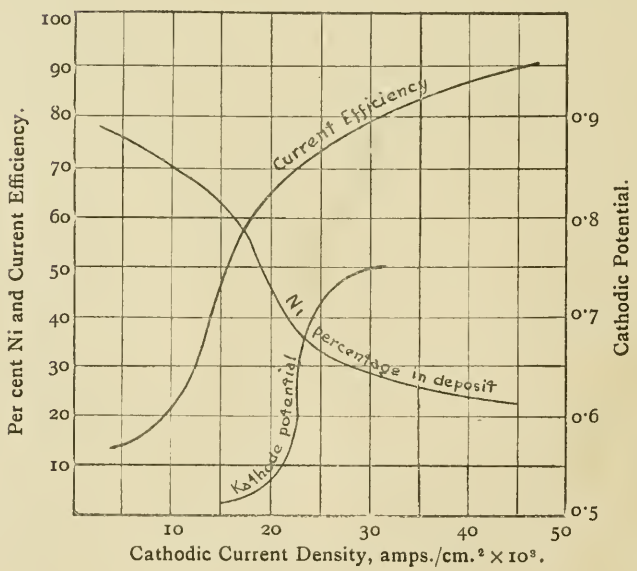


FIG. 2.

the fact which had almost at the same time been established by E. P. Schoch and A. Hirsch (*Journ. Am. Chem. Soc.*, 1907, xxix., 314), that from a solution which contains in addition to an excess of nickel sulphate some zinc sulphate, cathode deposits may be obtained at ordinary temperature which will be decidedly richer in zinc than in nickel. Treadwell's results were the following:—At ordinary temperature solutions, in which the nickel sulphate 0·5 N as regards the zinc sulphate and the nickel sulphate, and 0·01 N as regards the sulphuric acid. The percentage of nickel in the cathode deposit, the cathodic current efficiency, and the variation of the cathode potential with the current density are plotted in the diagram. It will be seen that the nickel percentage is very low even at small current density; the percentage decreases to a minimum, and rises very slowly afterwards. The current efficiency

also rises with increasing current density, from 90 per cent to 95 per cent at high density; thus little current is spent in the generation of hydrogen.

The same solution yields essentially different results at 80°, however, as the experiments plotted in Fig. 2 will show. In this case the deposits, as long as the current density is kept low, are rich in nickel, and resemble nickel in appearance. When the current density is raised, the nickel percentage of the deposit falls off, very rapidly at first, more slowly afterwards. The deposition of the alloy rich in Ni takes place at potentials at which, in the absence of zinc, the solution would have thrown down nickel only. When, however, with increased current density, the Ni percentage of the deposit is lowered and the alloys become richer in Zn, the cathode potential likewise rises suddenly to values approaching that required for the deposition of zinc. The current efficiency curve takes a similar trend. At low current density the efficiency remains below 20 per cent; the current is mainly spent in liberating hydrogen, therefore. When the cathode potential jumps up to that of base metals, with increasing current density, the current efficiency also rises rapidly.

The retardation phenomena occurring in the electrolysis of solutions containing zinc sulphate and ferrous sulphate

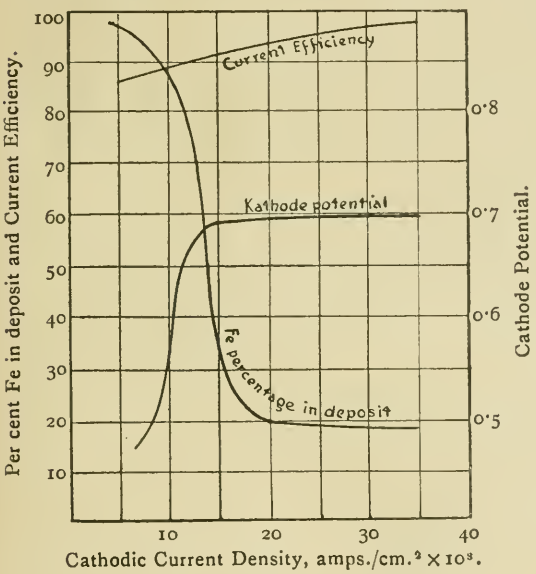


Fig. 3.

are somewhat more pronounced still, as W. von Escher has shown ("Dissertation," Dresden, 1912). It we start from solutions which are equally concentrated as to zinc and iron, the alloys deposited, not only at ordinary temperature, but also at 90°, at very small current density, consist predominantly of zinc. To obtain alloys rich in iron, at low current densities and high temperatures, is only possible when there is a decided excess of ferrous sulphate over the zinc sulphate. Fig. 3 exemplifies an experiment conducted at 90°; the solution was 0·01 N acid, and the ratio of Fe to Zn was 9 : 1·5. Although the temperature was high, it will be recognised the transition from deposits rich in Fe to deposits rich in Zn took place already at very low current density. The deposit potentials were, for the alloys rich in iron, those which (as resulted from special experiments) were required for the deposition of pure iron from solutions of ferrous sulphate of equal concentration. When, however, at higher current densities the transition-point to the deposits consisting essentially of zinc had been passed, the cathode potential assumed the value corresponding to pure zinc. The current efficiency was somewhat below 90 per cent at low current density, and a little above that value at high current density. Further experiments made at the same temperature (90°) showed that when the ratio Fe : Zn was varied in favour of iron, the transition-point from predominantly iron deposits to zinc deposits was shifted into the region of higher current density. In one series of measurements, in which the concentration ratio was Fe : Zn = 9 : 0·63, but which otherwise agreed with the former, the transition occurred only at the density 0·035 or 0·040 amp./cm.². On the other hand, any lowering of the temperature or an increase in the zinc concentration shifted the transition into the region of low current density or suppressed it altogether, the deposits remaining rich in zinc at all the current densities. The concentration of the hydrogen ions also has an influence upon the transition. In a solution of 0·01 N acidity and a concentration ratio Fe : Zn = 9 : 1, the transition was observed at the current density 0·022 amp./cm.² at 90°; in a neutral solution of the same concentration, however, the deposits were poor in zinc up to current densities of 0·040 amp./cm.². In this latter case the transition did not take place therefore. It could be produced, however, also in neutral solutions by raising the zinc concentration. With the concentration ratio Fe : Zn = 9 : 1·5, *e.g.*, the transition was observed at 90°, in neutral solution, between the current densities 0·020 and 0·025 amp./cm.². The zinc proportion of the cathode deposit, at which transition occurred, was 11 per cent, however, whilst 5 per cent sufficed with 0·01 N acidity to raise the potential to the value necessary for the zinc preponderance. The transition was thus more easily realised in the latter case, which is further indicated by the circumstance that a current density of 0·010 amp./cm.² was sufficient.

(To be continued).

ON THE ORIGIN OF SOLAR ELECTRICITY.*

By J. A. HARKER, D.Sc., F.R.S.

More than twenty years ago, in his presidential address to the Physics Section of the British Association at Edinburgh, when discussing solar phenomena, Professor Schuster (*Brit. Assoc. Report*, 1892, p. 635) said:—

"May not the periodicity of sun-spots and the connection between two such dissimilar phenomena as spots on the sun and magnetic disturbances on the earth be due to a periodically recurring increase in the electric conductivity of the parts of space surrounding the sun?"

Professor Hale (*Proc. Roy. Inst.*, xix., 621), in his Royal Institution lecture in 1909 on "Solar Vortices and Magnetic Fields," described the methods by which he had detected within the vortices, shown by the spectroheliograph to be present in sun-spots, magnetic fields of considerable strength. In discussing the probable origin of these fields, Hale says:—

"We know from Rowland's experiment that the rapid revolution of an electrically charged body will produce a magnetic field. Thus if a sufficient number of electrically charged particles were set into rapid revolution by the solar vortices, a magnetic field should result. What warrant have we for assuming the existence of charged particles in the sun?"

Some experiments made at the National Physical Laboratory during the past two years by Dr. G. W. C. Kaye (see Note 1) and the writer on the emission of electricity from hot bodies seem to have a distinct bearing on these problems. The application to cosmical phenomena of some deductions from these and a few hitherto unpublished further experiments forms the subject of the present paper.

It may be well briefly to recapitulate here the results

* From *Monthly Notices of the Royal Astronomical Society*, lxxxiii. No. 8.

attained. The first experiments dealt with the electric conductivity of the space inside a carbon-tube resistance furnace heated by alternating current. A pair of small insulated exploring electrodes of carbon projected into the furnace at opposite ends, and were connected with a battery of a few volts and a suitable current-measurer. It was found that, as the furnace was gradually heated from room-temperature, the resistance of the interior space remained practically infinite until a temperature of about 1400° C. was reached, when the resistance commenced to fall rapidly. The curve showing the current between the two exploring electrodes was exponential in character.

It was further found that, on removing the battery, and therefore in complete absence of all applied potential, a transient electric current could be obtained by keeping one of the electrodes in a fixed position in the furnace, and heating or cooling the other by moving it in or out of the hot region. The direction of the current indicated a negative (Note 2) emission from the hotter to the colder surface across the gap (Note 3).

Ionisation currents up to about 3 ampères at over 3 volts were thus obtained from a quite small apparatus, having a working electrode-area of only a few square centimetres. If both electrodes are kept stationary in the furnace, and one is maintained permanently hot, and the other, by means of water-cooling, kept at a much lower temperature, continuous currents of the order of an ampère can be obtained without the application of any potential.

In a later form of the experiment a thin rod of carbon about 15 cm. in length was heated to a very high temperature by low-voltage alternating current; an ionisation current of over 3½ ampères was emitted by the surface of the rod to a comparatively cool insulated carbon tube surrounding it, the current-density in this case exceeding 0·1 ampère per sq. cm. at atmospheric pressure.

The current appears to be associated with the emission from the hot carbon surface of negatively charged particles. As all the experiments were made at atmospheric pressure, it would seem that these particles must consist almost entirely of sputtered *matter*, and that "corpuscles," whose unencumbered range at such pressures would be extremely small, do not here play the great part in the phenomena they do in high vacua. The evidence to hand in support of this view is discussed in the two memoirs referred to.

In view of the interest of these results obtained with carbon, preliminary experiments on the volatilisation and electric emissivity of a number of metals were made, mostly in nitrogen, at pressures from a few millimetres upwards. The metals were heated by alternating current, and no applied potential was employed. It was found that positive electricity was emitted at temperatures from 1000° to 1400° C. With those metals which melt within this range, a sudden and marked increase in the positive current occurred at the liquefying-point.

At higher temperatures negative electricity predominates, and its quantity increases rapidly with the temperature. With strips of pure iridium, melting between 2300° and 2400° C., which was the metal found to give by far the largest emission, the negative current attained nearly 1-10th of an ampère at the melting-point, the radiating surface being approximately 4 sq. cm. With iron transformer-plate melting at about 1500° C., a large emissivity was often obtained, but with this metal it was found impossible to repeat any given set of conditions sufficiently accurately to obtain even approximately identical results in successive experiments. The negative currents appear to be always associated with considerable sputtering of the metal, and are probably a consequence of some reaction between the metallic surface and the surrounding gas. With carbon the nature, and to some extent also the pressure, of the gaseous atmosphere surrounding the radiating material exerted an influence on the emissivity at the higher temperatures, and with the metals the temperature at which the positive emission changed sign seemed to be greatly influenced by the presence or absence of minute quantities of impurity in the nitrogen atmosphere surrounding the specimen.

From these experiments, and from the known facts regarding the emissions from other materials such as refractory oxides, it would appear that *most substances capable of withstanding a high temperature emit electricity when strongly heated, and that their emissivity when once established increases rapidly with rise of temperature.*

It was obvious from all the experiments that the electric conductivity inside a hot carbon-tube furnace, as evidenced by the ionisation currents produced, was very large, and it is of interest to compare the gaseous conductivity thus manifested with other examples.

A hard Röntgen-ray tube has an apparent resistance of megohms. A quartz mercury-lamp of the usual type has a resistance when running of the order of 50 ohms. In many of these experiments, even with quite small furnaces, the gaseous resistance was measured to be less than 1 ohm at temperatures above 2000° C.; while in one case in a large furnace, where the temperature was pushed to over 3000° C., the apparent resistance fell to microhms, or at any rate to something comparable with that of the graphite rods and of the copper cables forming the rest of the electric circuit. This would mean that *the conductivity of the ionised space was of the same order as if it were filled with mercury or a liquid electrolyte.*

In none of the emission experiments either on carbon or metals up to their melting-point was there any evidence of discontinuity in the law of rapid increase in emissivity with temperature, which was found to hold for the solid substance. Some of the metals, however, showed on melting a marked *increase* in the emission at the moment of fusion.

A word or two may be said here as to the probable velocity and size of the particles which apparently act as carriers in these experiments. In many instances no electric potential was applied, and it seems, therefore, that the particles owe their velocity of emission solely to the temperature. For carbon at 3000° C., according to J. J. Thomson's theory, this velocity should be about 3×10^7 cm. per second, or about a thousandth of that of light, a speed which, compared with that of some corpuscles, is very slow. But, unlike corpuscles, the particles can travel considerable distances in gases even at atmospheric pressure.

If, as we are inclined to believe, it should ultimately prove to be the case that the ionisation currents are carried chiefly by these particles, we have then a means of deducing fairly readily the relation of their charge to their mass (e/m).

An experiment to this end on iridium in nitrogen at 20 mm. pressure, the strip being at a temperature of 1360° C. (black-body), gave the result that the average number of iridium atoms contained in the particle carrying a single negative charge was 1200. In this case, therefore, the mass of the carrier is roughly 5×10^8 times greater than that of a corpuscle, whose mass is 1-1800th of that of a hydrogen atom.

Turning now to the phenomena presented in the sun, it would seem in the light of these facts impossible to avoid the conclusion that *the solar atmosphere is a highly conducting medium.* The most modern determinations of solar temperatures all give values between 5600° and 6000° Abs. (Note 4), estimates much lower than those formerly accepted. From spectroscopic evidence it has been established beyond dispute that iron forms one of the principal constituents of the sun, and carbon a not unimportant one both of the sun and of many stars. For present purposes we will limit our considerations to a discussion of the probable influence on the solar atmosphere of the presence of these two elements.

Iron at its melting-point gave negative currents up to about 15 micro-ampères per sq. cm. in nitrogen at 9 mm. pressure; a rise of temperature of only 60° C. serving to double the current-density over this part of the range.

Even assuming no further increase of emissivity with rise of temperature beyond the melting-point, the current emitted per square kilometre of the area of the photosphere would even on this basis attain 150,000 ampères.

Considering next the case of carbon, if we assume the validity for extrapolation purposes of any such law of increase of conductivity of the space inside a carbon furnace, as that deducible from the data plotted in Fig. 4 of the paper alluded to (Harker and Kaye, *loc. cit.*; *Proc. Roy. Soc.*, 1912, lxxxvi., A, 385), we find that at a temperature far short of that of the sun the conductivity becomes greater than that of any known substance.

Suppose however that, to be on the safe side, we assume in the sun no further increase in emissivity above the figure of 0·1 ampère per sq. cm., actually measured at a temperature approximately 3000° C., this would be more than ample to account for the enormous currents which recent considerations have rendered it probable are circulating in the solar atmosphere.

Hale has shown that it is highly probable that intense magnetic fields of from 2000 to 5000 C.G.S. units are found in sun-spots, and that there is also a general magnetic field of much less intensity existing over the whole body of the sun. Assuming that the circuit producing the field in a spot consists of a single turn, calculation shows that currents of the order of ten million million ampères are required (Note 5).

But at the rate of 0·1 ampère per sq. cm., which is 1000 million ampères per sq. kilo., an area of only 100 × 100 kilometres would alone be required to generate this current, assuming carbon as its source.

As to the mechanism by which the currents *are actually generated* in the solar atmosphere, our present knowledge is very meagre, particularly in view of the great uncertainties as to the physical state of the elements in the sun at the prevailing pressures, also as regards temperature distribution over the surface of the photosphere, and radially outwards through the solar atmosphere. Of the several alternative processes by which the enormous local currents circulating round a sun-spot *might* be generated, that favoured by Hale, the revolution of large numbers of the charged particles by the solar vortices, seems least open to objection.

One obvious direction for further research, before the data here discussed can be properly applied to the elaboration of an electrical solar theory, is the continuation of the experiments on metals beyond their melting- and boiling-points. Indeed, a few preliminary experiments in this direction have already been made. One obstacle at present in the way of their successful completion is to find a material suitable for the construction of the necessary vessels, which is at the same time sufficiently inert and refractory, and which does not itself emit electricity over the temperature range to be studied.

Some indirect evidence on this question of the behaviour of vapours is, however, to hand. It was found that in the experiments with carbon, when a new carbon tube of ordinary commercial quality was heated for the first time, the emission at temperatures in the neighbourhood of 2000° C. was always four or five times as great as in later heatings to the same temperature. It was always observed that, during the first heating in a current of inert gas, the impurities in the carbon, consisting mostly of iron and silicon, are distilled out of the body of the material and carried off in the stream of gas. It was ascertained that this comparatively volatile material all leaves the carbon surface carrying a charge.

In bringing the foregoing facts to the notice of astronomers and cosmical physicists, the writer is fully conscious of many criticisms which may be urged against the conceptions here outlined. But in view of the discoveries of Hale and others, and the consequent interest now being taken in solar phenomena, a presentation of the data even at this early stage in their investigation may not be considered premature.

It may ultimately prove to be the case that such evidence as is here presented, if further supported, may be considered by the authorities as sufficiently conclusive for presuming the existence in the solar atmosphere in very large numbers of electrified particles, by the movements of which enormous currents are generated. Very probably these particles have a mass and velocity widely different from those of corpuscles, the bodies hitherto considered almost exclusively in discussions as to solar currents and magnetism (Note 6). It may therefore, as a consequence, be necessary for cosmical physicists to revise some of their arguments as to the inter-relations of terrestrial and solar magnetic phenomena.

In conclusion, I desire to express my thanks to the Astronomer Royal, to Professor Fowler, and to Dr. W. J. S. Lockyer for their help in references to data and literature.

Notes.

1. Harker and Kaye, "On the Emission of Electricity from Carbon at High Temperatures," *Proc. Roy. Soc.*, 1912, lxxxvi. [A], 379; "On the Electric Emissivity and Disintegration of Hot Metals," *Proc. Roy. Soc.*, June 19, 1913.

2. Positive emissions were obtained with new carbon at low temperatures on first heating, and were probably associated with the expulsion of the first traces of the contained impurities.

3. The hot fixed electrode, being in thermal equilibrium with its surroundings, takes no part in the generation of these currents. The latter may be considered as entirely due to the alternating temperature differences between the surface of the movable electrode and the hotter and colder parts of the furnace-wall immediately surrounding it. It has been conclusively established that the ionisation currents are *not* due to thermo-electricity, or to any rectifying action of the carbon on the alternating currents used for heating the furnace. Many of the effects have been obtained in experiments where the heat-supply has been furnished from non-electrical sources.

4. For example, Abbot, "Measurements on Mount Wilson and Mount Whitney," 5840° Abs. Calculated from an assumed value of Stefan's constant. Also Harker and Blackie, "National Physical Laboratory Report," 1908. 5610° Abs. By total radiation pyrometer directly standardised up to arc temperature, assuming atmospheric absorption 29 per cent.

5. The Astronomer Royal and Mr. Maunder kindly supplied the necessary dimensional data for the spots to enable this computation to be made.

6. See, for example, Schuster, *Proc. Roy. Soc.*, 1911, [1], p. 44; and Birkeland, "The Norwegian Aurora Polaris Expedition," vol. i.; "On the Cause of Magnetic Storms and the Origin of Terrestrial Magnetism," pp. 151 *et seq.*

Colloidal Properties of Hæmoglobin. — Filippo Bottazzi.—The author has prepared pure hæmoglobin by dialysis, when after about five months it is obtained as a red precipitate which refracts light strongly, During dialysis 95 per cent of the hæmoglobin is transformed into meta-hæmoglobin. When perfectly dialysed the latter coagulates at 47—53°. If it is imperfectly dialysed, or in presence of a trace of alkali it becomes opalescent and turbid at that temperature. In presence of an excess of alkali or acid and in absence of neutral salts hæmoglobin is not coagulated by heat. When exposed to the action of an electric field meta hæmoglobin migrates from cathode to anode, and hence is an electro-negative colloid. The electric conductivity is high. The very low coagulation point suggests that during the transformation of oxyhæmoglobin into meta-hæmoglobin it undergoes a process of polymerisation or condensation.—*Atti della Reale Accademia dei Lincei*, vol. xxii. [ii.], No. 4, 1913.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

SOME NEW EXPERIMENTS CONCERNING SPRINGS.

In spite of all the researches that have been made about the mysterious power of spring-finders the problem of source finding remains obscure. Fifteen years ago, in the Laboratory of Marey, Dr. Marage undertook some experiments the object of which was to determine what was true in the phenomenon of the spring finder's wand. These experiments, of a psycho-physiological order, are excessively long, and all those who have studied these questions know the difficulties that are met with before being able to make any serious observations. Having established that this phenomenon seems to be found in a great number of subjects, about one out of ten, Dr. Marage resolved to have recourse preferably to amateurs, absolutely disinterested as to the positive or negative success of the search for springs and having scientific culture. He thus entered into relation with some engineers, and it is the exceedingly interesting results of these experiments that Professor d'Arsonval has presented before the Academy of Sciences. The experiments were tried in Tunis on the side of the roads 38 from Enfidaville to Kairourou and 3 from Enfidaville to Zaghouan. They were made by M. Laudesque, road surveyor, and controlled by civil engineers. As the wand gave him no result, M. Laudesque made use of the pendulum formed, as is well known, by a little sphere or a small conical cylinder suspended at the end of a thread. He was able to determine nine springs of water and to indicate beforehand the depth of the water varying from five to nineteen metres. Soundings were made at the nine points; water was always found, and the depth was recognised as exact at seven points. So there were two errors; the first at the 21st kilometre of the road 38, where water was announced at 13 metres and found at 23 metres, and the second at the 19th kilometre of the road 3, where water was announced at 18 metres and found at 3 metres. The error of depth seems to be due, in the first case, to an incomplete examination of the ground, and in the second case to the width of the subterranean current. In these kinds of researches the negative experiments being often more instructive than the positive, M. Laudesque tried to discover the explanation of the errors he had committed. Dr. Marage thinks that these experiments have the advantage of not giving rise to any criticism on the part of professional spring-finders, who, indeed, contest the value of the results obtained on water channels. Moreover, thanks to the service of roads and bridges, which possesses the means of taking soundings, these researches may be continued in our African colonies. M. Laudesque is quite disposed to give his services to the commission appointed by the Academy of Sciences, composed of Messrs. Armand Gautier, Dastre, Violle, and Douville, in order to make under its direction whatever experiments may be considered useful. In any case the experiments of M. Laudesque are, according to Dr. Marage, the first really well-conducted experiments made on spring-finders, as well as the first having given practical and indisputable results.

THE WORK OF THE INTERNATIONAL BUREAU OF WEIGHTS AND MEASURES.

The fifteenth volume of the memoirs and work of the International Bureau of Weights and Measures has just been presented to the Academy of Sciences by M. Gaston Darboux, perpetual Secretary. We have still fresh in our memory the fine studies of MM. Michelson and Benoit, who have made known to about a millionth degree the fundamental wave-length which the classical work of Rowland had left uncertain to about a 30 thousandth degree. Still further perfecting these methods, MM. Benoit, Fabry, and Perot have been able to simplify, in an enormous proportion, the process of the reduction of the metre to the greatest standard in wave-length. They have also managed to be able to guarantee about the ten-millionth in the values announced to-day, and which by a lucky hazard concord likewise at about the ten millionth with those that were given twenty years ago. M. Ch. Ed. Guillaume gives an account of the determination of standard measures from 1896 to 1904. Lastly the work of the fifth general conference of Paris is resumed at the end of the volume. It was at this conference that the results relative to the mass of the cubic decimetre of water were communicated as well as those concerning the values of the fundamental wave-length. The metrical carat at present accepted everywhere received the first official sanction at this conference.

THE GIACOBINI COMET.

M. Giacobini, astronomer of the Paris Observatory, in a notice presented before the Academy of Sciences by M. Bailland, director of the Observatory, has just made known the elliptical elements of the comet 1913-E. The calculations with the observations made at the observatories of Bamberg, Algiers, and Paris prove without the slightest doubt that this comet is the same as that discovered by Giacobini in 1900. The duration of the revolution of this comet is not more than six years and 464 millionths of a year.

THE EFFECTS OF GUANINE.

Fresh researches on the antagonism of the influences exercised by guanine and andrealine on the constitution have just been made by Professor Desgrez, of the Faculty of Medicine, and by M. Dorléans, In their paper presented by M. d'Arsonval, the two seekers establish that guanine increases the resistance of animals against the toxic action of andrealine, and that it decreases the amount of sugar elimineted under the influence of this substance, so that only traces of it are to be found.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 13th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows :—

"*The Preparation of Eye-preserving Glass for Spectacles.*" By Sir WILLIAM CROOKES, O.M., F.R.S.

Since March, 1909—in connection with the Glass Workers' Cataract Committee of the Royal Society—I have been experimenting on the effect of adding various metallic oxides to the constituents of glass in order to cut off the invisible rays at the infra-red end of the spectrum, and thus to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workmen, without obscuring too much light or materially affecting the colours of objects seen through the glass when fashioned into spectacles.

Single metals were at first tried in varying quantities to see if from the colour and properties communicated to the glass they were worth further examination. Each specimen is cut and polished into a plate 2 mm. thick. The plate so prepared is first put into the radiometer balance to find the percentage of heat cut off. It is then tested in the spectrum apparatus to ascertain the upper limit of transmission of the ultra-violet rays, next it is tested in Chapman Jones's opacity meter to estimate the percentage of luminous rays transmitted, and finally the colour is registered in a Lovibond's tintometer.

The following elements were selected as likely to be worthy of further experimentation by combining the metals, two, three, or four at a time, in one glass so as to enable the advantages of one to make up for the shortcomings of another :—Cerium, chromium, cobalt, copper,

iron, lead, manganese, neodymium, nickel, praseodymium, and uranium.

Whilst bearing in mind that the chief object of this research is to find a glass that will cut off as much as possible of the heat radiation, I have also attacked the problem from the ultra-violet and the transparency points of view. Taking each of these desiderata by itself I have succeeded in preparing glasses which cut off over 90 per cent of heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be capable of use as spectacles. But I have not been able to combine in one specimen of glass these three desiderata in the highest degree. The ideal glass which will transmit all the colours of the spectrum, cutting off the invisible rays at each end, is still to be discovered.

As far as transparency, however, is concerned it will not be an unmixed advantage for the sought-for glass to be quite clear and colourless. The glare of a strong light on white cliffs, expanses of snow, electric light, &c., is known to be injurious to the eye, and therefore a tinted glass combining good obstruction to the heat radiation and ultra-violet rays is the best to aim for.

For ordinary use, when no special protection against heat radiation is needed, the choice will depend on whether the ultra-violet or the luminous are most to be suppressed; or whether the two together are to be toned down. Ordinarily the visible spectrum is assumed to end at the Fraünhofer line K, λ 3933, but light can easily be distinguished some distance beyond by the naked eye. It may therefore be considered that the ultra-violet rays which are to be cut off on account of their possible injurious action are those of shorter wave-lengths than, say, λ 3700. Many glasses have been prepared for this purpose all of which are opaque to rays shorter than λ 3700. The colours are pale green, yellow, and neutral; they transmit ample light so that a choice of tints is available to suit individual taste.

Glasses which are restful to the eyes in the glare of the sun on chalk cliffs, expanses of snow, or reflected from the sea of yellow, green, and neutral tints have also been prepared which have the advantage of cutting off practically all the ultra-violet rays and also a considerable amount of the heat radiation.

"*An Inversion-point for Liquid Carbon-dioxide in regard to the Joule-Thomson Effect.*" By Prof. A. W. Porter, F.R.S.

"*Negative After-images and Successive Contrasts with Pure Spectral Colours.*" By Prof. A. W. Porter, F.R.S., and F. W. Edridge-Green, M.D.

This paper is a rejoinder to the criticisms made by Prof. Burch to our previous paper. We have repeated our experiments, taking the most minute precautions to avoid all stray light with the same results as before. The most important result is that a negative after-image of an approximately complementary colour is obtained in the total absence of stimuli which would cause such colour.

"*The Positive Ions from Hot Metals.*" By Prof. O. W. Richardson, F.R.S.

"*The Diurnal Variation of Terrestrial Magnetism.*" By G. W. Walker, F.R.S.

The paper deals with observational data with regard to the diurnal variation of terrestrial magnetism collected from nine observatories.

The data are presented in terms of the Fourier coefficients of the twenty-four hour and twelve hour terms for the geographical components to north, west, and vertical (downwards).

It is noted that the data give strong support to Dr. Schuster's formulæ (*Phil. Trans.*, 1908) for the magnetic potential of diurnal variation as derived from the west component; but the magnetic potential so determined does not give the proper numerical values for the north component as observed.

Two courses are open:—(1) To proceed to higher harmonics; (2) to suppose that the phenomena do not depend entirely of local station time. (1) is discarded partly on account of the trouble of numerical labour, but chiefly because it is likely to lead to unsatisfactory values at the equator or the poles. (2) is tried tentatively and potential functions of simple type are formed which give a general correspondence with the data from these nine stations. More extended data may modify the numerical coefficients.

Without confining oneself to any special theory, the mode of genesis of such potential functions as are suggested by the observations can be specified as related to differential solar action. This is essentially a reversal of Schuster's analytical method. It may stop whenever the data have been accounted for, and thus lead back to the differential conductivity arising from solar action required in Schuster's theory.

The data for vertical force are shown to be in general agreement with Schuster's conclusion that the primary source of variation is of epigene origin.

"*A Suggestion as to the Origin of Black Body Radiation.*" By G. W. Walker, F.R.S.

The paper first shows that a function of dynamical form can represent the data with regard to radiation quite as well as the formula proposed by Planck.

If the emission at temperature θ in the range of wave-length $\delta\lambda$ is $\phi(\theta, \lambda)\delta\lambda$; then the form—

$$\phi(\theta, \lambda) = k\theta^5 \left(\frac{\lambda\theta}{\lambda^2\theta^2 + a^2} \right)^4$$

satisfies—

1. Stefan's law that the total radiation varies as θ^4.
2. Wien's law that the maximum radiation at any temperature occurs at λ_m, where $\lambda_m\theta$ = constant.
3. The maximum radiation at this wave-length λ_m varies as θ^5.
4. The radiation for great wave lengths takes Lord Rayleigh's form, varying as $\theta\lambda^{-4}$.
5. It agrees with great closeness with Lummer and Pringsheim's results for short wave-lengths.

It is next shown that the equations of motion for an electron obtained by the author (*Phil. Trans.*, 1910) lead to an emission expression of this quartic type, but in a more general form, which could probably be fitted with the experimental data.

The inference is drawn that the radiation is probably determined by the joint action of a positive and a negative charged particle in stationary orbital motion.

The experimental data are thus brought into accordance with the established principles of dynamical and electrodynamical theory.

CHEMICAL SOCIETY.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Whinfield, Salcombe, S. Devon, Sept. 16th, 1913.

Gentlemen,—I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1914, which is submitted for publication in the Society's *Transactions* and *Proceedings*, as hitherto.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report, but, in accordance with the resolution passed at the Eighth International Congress of Applied Chemistry, it is not proposed to make any change in the official table of atomic weights until the meeting of the next Congress in 1915.

Apart from this, the work of the past year has not shown any necessity for any addition to the existing list of Atomic Weights, or for any substantial alteration in the values last published.

It is accordingly recommended that the table accompanying the Report for 1913 should be reprinted as it stands.

I have appended the signatures of Professors Ostwald and Urbain as desired by them.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, the Chemical Society, London.

Annual Report of the International Committee on Atomic Weights, 1914.

At the Eighth International Congress of Applied Chemistry, held in New York in September, 1912, a resolution was passed favouring less frequent changes in the official table of atomic weights. Such changes are sometimes embarrassing to technical chemists, and the resolution adopted expressed a desire that the table for 1913 should remain, for legal and commercial use, the official table until the next Congress convenes, in 1915. With this wish the Committee can easily comply; at least, in its essential features, for changes which affect the industrial chemist are not likely to be important, and the text of each annual report will give all the refinements of data which may be needed in theoretical discussions. Only such changes in the table as seem to be absolutely necessary need be made during the next two years, and that they should seriously affect the values in common use is highly improbable.

Since the annual report for 1913 was prepared, a number of important memoirs on atomic weights have appeared, which may be summarised as follows:—

Nitrogen.—Scheuer (*Anzeiger Wien Akad.*, 1912, xlix., 36), from analyses of nitrogen trioxide and tetroxide, and from measurements of ratios connecting the oxides of nitrogen, finds N = 14·008 as the mean of five series of determinations. He also determined the densities of ammonia and of sulphur dioxide, obtaining results in accordance with earlier investigations. The value assigned to N varies from the rounded-off figure given in the table by only 1 part in 7000.

Chlorine.—By the synthesis of NOCl, by the direct union of nitric oxide and chloride, Wourtzel (*Comptes Rendus*, 1912, clv., 345) finds Cl = 35·4596, when N = 14·008. He also (*Comptes Rendus*, 1912, clv., 152) determined the density of nitrosyl chloride, and found the weight of the normal litre to be 2·9919). From this he deduced a molecular weight of 65·456, which is probably too low. From the ratio between ammonia and hydrochloric acid, re-measured by Baume and Perrot (*Comptes Rendus*, 1912, clv., 461), the authors found Cl = 35·463, an unusually high value. None of these new determinations warrants any change in the accepted figure for chlorine.

Bromine.—By the direct synthesis of hydrobromic acid from weighed quantities of hydrogen and bromine, Weber (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1294) finds Br = 79·3066 when H = I. With O = 16, the value for bromine becomes 79·924. The accepted value differs from this by only 1 part in 20.000.

Phosphorus.—Baxter and Moore (*Journ. Am. Chem. Soc.*, 1912. xxxiv., 1644), from analyses of phosphorus trichloride, find P = 31·018, in good agreement with previous determinations. This is slightly lower than the value given in the table.

Iron.—By the reduction of ferric oxide in hydrogen, Baxter and Hoover (*Journ. Am. Chem. Soc.*, 1912 xxxiv., 1657) finds Fe 55·847.

Cadmium.—The electrochemical equivalent of cadmium has been determined by Laird and Hulett (*Trans. Am. Electrochem. Soc.*, xxii., 385), who precipitated cadmium and silver simultaneously in an electric current. From the data given, the atomic weight of cadmium is 112·31, a low value, but one in accord with the previous work of Hulett and Perdue on cadmium sulphate. The investigation is to be continued with the chloride.

Tellurium.—The supposed complexity of tellurium has been re-investigated by Dudley and Bowers (*Journ. Am. Chem. Soc.*, 1913, xxxv., 875), with negative results. They attempted to determine the atomic weight by the basic

International Atomic Weights. (1914).

		O = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	22·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0

		O = 16.
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

nitrate method, which they found to be unsatisfactory. A series of syntheses of the tetrabromide gave Te = 127·479.

Uranium.—From calcinations of uranyl nitrate to uranium dioxide, Lebeau (*Comptes Rendus*, 1912, clv., 161) found U = 238·54. Œchsner de Coninck (*Comptes Rendus*, 1912, clv., 1511), by calcination of uranic oxalate, obtained variable results, in mean, U = 238·44.

Scandium.—Atomic weight re-determined by Meyer and Goldenberg (Chem. News, 1912, cvi., 13), who employed the sulphate method. In mean, Sc = 44·14, in agreement with the accepted value. The higher figure given by Meyer and Winter was due to the presence of thoria in the material employed.

Yttrium.—Two determinations of the atomic weight by Meyer and Wuorinen (*Zeit. Anorg. Chem.*, 1913, lxxx., 7) gave Yt = 88·6. The sulphate method was used. Egan and Balke (*Journ. Am. Chem. Soc.*, 1913, xxxv., 365), in a preliminary study of the ratio between yttrium chloride and yttria, found Yt = 90·12. As their research is to be continued, it would be unwise to use either of these investigations as a basis for changing the table. The lower of the two values appears to be the more probable.

Ruthenium. — Vogt (*Sitzungsber. phys. med. Soz. Erlangen*, xliii., 268), from reductions of ruthenium dioxide, finds Ru = 101·63.

Palladium.—Determinations of atomic weight by analysis of palladiammonium chloride have been made by Shinn (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1448). The mean value obtained was Pd = 106·709, but the individual determination varied more than is satisfactory. Shinn supposes that the chloride is less definite than it has been assumed to be.

Radium.—From analysis of radium bromide, Hönigschmid (*Monatsh.*, 1913, xxxiv., 283) finds Ra = 225·97, in confirmation of his former analysis of the chloride. The discordance between this value and the higher value obtained by others is unexplained. The presumption is in favour of Hönigschmid's determination, but a change in the table may well be deferred until more evidence is available.

The accompanying table is that of 1913, unchanged.

(Signed) F. W. Clarke.
W. Ostwald.
T. E. Thorpe.
G. Urbain.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions* :—

212. "*Viscosity of Cellulose Nitrate Solutions.*" By Frank Baker. (*Trans.*, 1913, 1653).

The viscosities of solutions in various solvents of different concentrations of cellulose nitrates have been determined. The relation $\gamma = \gamma_0(1 + ac)^k$ was found to express the connection between the concentration of cellulose nitrate (c) and the viscosity. Comparison between the results obtained with different solvents suggests that the values of the constants a and k depend on the solvent power of the liquid for nitrocellulose.

The viscosity of solutions of nitrates of mercerised cellulose suggests that cellulose and mercerised cellulose are not identical, but that cellulose is degraded in the process of solution in ammoniacal copper oxide.

The influence of molecular attraction on physical properties is discussed, and association in liquids ascribed to increased molecular attraction.

213. "*Geranyl Chloride.*" By Martin Onslow Forster and David Cardwell. (*Trans.*, 1913, 1338).

Geranyl chloride has been prepared by the action of thionyl chloride on a mixture of geraniol and pyridine, and appears to be identical with linalyl chloride; reasons are given for regarding the $C_{10}H_{17}$-nucleus as being that of geraniol rather than the tertiary linanyl group. The *nitrosate*, $C_{10}H_{17}O_4N_2Cl$, melting at 101°, is a convenient derivative by which to identify geranyl chloride, which has a distinct odour of hops, and boils at 103°/14 mm.

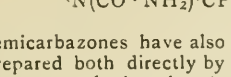
The *hydrocarbon*, $C_{10}H_{16}$, produced along with geranyl chloride, boils at 174—176°/763 mm., and yields a *nitrosate*, melting at 131°, whilst the *hydrocarbon*, $C_{10}H_{18}$, prepared by reducing geranyl chloride, boils at 161°/763 mm., and yields a *nitrosate* melting at 95°. *Geranylamine*, $C_{10}H_{19}N$, boils at 105°/19 mm., and forms definite derivatives with the usual agents.

214. "*A New Method of Preparing* m-*Chlorobenzoic Acid and the Investigation of its Hydroxylamine Salt.*" By Wilhelm Gluud and Richard Rempf. (*Trans.*, 1913, 1530).

m-Chlorobenzoic acid is prepared by heating benzoic acid with *aqua regia* on a water-bath, the chloro-acid being separated from the crystalline mass by means of its calcium salt. The hydroxylamine salts of *m*-chlorobenzoic and benzoic acids were also prepared and examined, especially with reference to their solubility and their behaviour on heating. Both salts are easily converted into the corresponding ammonium salts, which readily dissociate into their components, the *m*-chlorobenzoate apparently more readily than the benzoate.

215. "*Contributions to our Knowledge of Semicarbazones.* Part III. *Action of Heat on the Semicarbazones of Phenyl Styryl Ketone and the Preparation of the Corresponding Phenylsemicarbazones.*" By Isidor Morris Heilbron and Forsyth James Wilson. (*Trans.*, 1913, 1504).

The authors have investigated the action of heat on the phototropic semicarbazones derived from phenyl styryl ketone (compare *Trans.*, 1912, ci., 1482). Both semicarbazones yielded, as main product, an isomeric compound melting at 189°, apparently cyclic in structure, for which the formula—



is suggested.

The phenylsemicarbazones have also been investigated, having been prepared both directly by the interaction of phenyl styryl ketone and phenylsemicarbazide, and also by the action of boiling aniline on the original semicarbazones. The course of the latter action has been found to depend on the duration of the heating with aniline, prolonged heating producing from both semicarbazones a compound melting at 169°, and apparently, as deduced from spectrographic evidence, analogously constituted to the substance melting at 189°. On the other hand, five minutes' heating with aniline produces colourless phenylsemicarbazones, each semicarbazone yielding its respective phenyl derivative.

These phenylsemicarbazones are strongly phototropic, becoming intensely yellow in light, whilst their solutions show thermotropic properties. The action of sodium ethoxide on the phenylsemicarbazones produces the same effect as light, yellow stereoisomerides being formed.

Various attempts were made to hydrolyse the phenylsemicarbazones, but these only resulted either in a partial conversion of the one stereoisomeride into the other or in the formation of the cyclic compound melting at 189°.

216. "*Contributions to the Chemistry of the Terpenes.* Part XVI. *The Oxidation of Bornylene with Hydrogen*

Peroxide." By Geoege Gerald Henderson and William Caw. (*Trans.*, 1913, 1543).

Bornylene, in solution in acetic acid, is slowly oxidised by hydrogen peroxide, with the production of a mixture of free acids and esters. The acids were found to be (1) camphenanic acid, $C_9H_{15}\cdot CO_2H$ (m. p. 95°); (2) the isomeric *iso*camphenanic acid (m. p. 74°); and (3) a liquid *acid*, which, from the analysis of its *methyl* ester and *silver* salt, appears to have the formula $HO\cdot C_8H_{12}\cdot CO_2H$. When distilled under diminished pressure this liquid acid is converted into a crystalline unsaturated *acid* (m. p. 80°), which has not been further examined.

The mixture of esters was separated by steam distillation into a volatile and a non-volatile part. The former yielded on hydrolysis (1) acetic acid and, in much smaller quantity, the three acids already mentioned; and (2) a mixture of two alcohols of the formula $C_{10}H_{17}\cdot OH$. The alcohol present in largest quantity proved to be borneol, whilst the other was identified as *epi*borneol.

The non-volatile esters when hydrolysed gave (1) acetic acid with much smaller quantities of the other acids, and (2) a mixture of two isomeric *alcohols* of the formula $C_{10}H_{18}O_2$. These alcohols are crystalline solids, which melt at 247—248° and 235—236° respectively; the quantities hitherto obtained were not sufficient to permit of a satisfactory examination of these compounds.

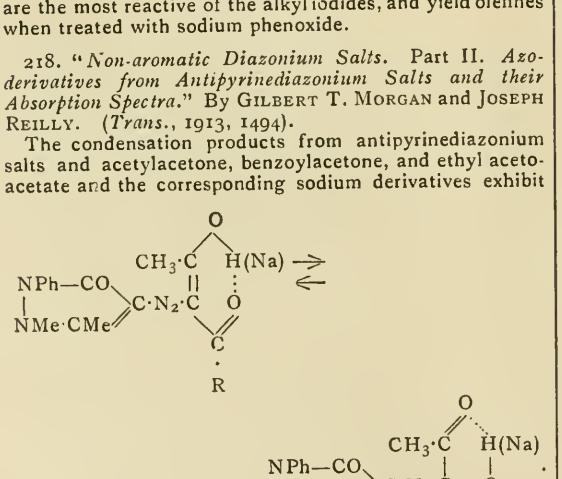
The formation of camphenanic and *iso*camphenanic acids from bornylene is of particular interest, because these acids have already been obtained by oxidising camphene with hydrogen peroxide (compare *Trans.*, 1911, cxcix., 1539). Thus further evidence is afforded of the very close similarity between the molecular structure of bornylene and that of camphene.

217. "*Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution.* Part II. iso-, sec.-, *and* tert.-*Alkyl Iodides.*" By David Segaller. (*Trans.*, 1913, 1421).

The reactivities of *iso*butyl, *iso*amyl, *iso*propyl, *sec.*-butyl, *sec.*-amyl, *sec.*-hexyl, *sec.*-heptyl, *sec.*-octyl, *tert.*-butyl, and *tert*-amyl iodides with sodium phenoxide in alcoholic solution have been measured. Allyl iodide was also included to give some indication of the effect of unsaturation. *iso*Compounds are much less reactive than the normal primary isomerides, whereas the normal secondary iodides are only slightly less reactive than the normal primary iodides. The reactivity decreases gradually with increase in molecular weight. The tertiary iodides are the most reactive of the alkyl iodides, and yield olefines when treated with sodium phenoxide.

218. "*Non-aromatic Diazonium Salts.* Part II. *Azo-derivatives from Antipyrinediazonium Salts and their Absorption Spectra.*" By Gilbert T. Morgan and Joseph Reilly. (*Trans.*, 1913, 1494).

The condensation products from antipyrinediazonium salts and acetylacetone, benzoylacetone, and ethyl acetoacetate and the corresponding sodium derivatives exhibit



very similar ultraviolet absorption spectra, their extinction curves being characterised by one persistent band comparable with the band shown by the 8-diketones themselves and their metallic derivatives. It is therefore suggested that these condensation products and their sodium compounds are azo-derivatives, having the accompanying co-ordinated configuration.

The corresponding azo-8-naphthylamine and its derivatives were also examined spectroscopically.

219. "*The Ten Stereoisomeric Tetrahydroquinaldinomethylene Camphors.*" By William Jackson Pope and John Reed. (*Trans.*, 1913, 1515).

The *d*- and *l*-tetrahydroquinaldines condense with the *d*- and *l*-oxymethylene camphors, yielding four simple optically active tetrahydroquinaldinomethylene camphors; any two of these latter compounds are capable of combining together to form a stable solid double compound. There are thus obtainable four partly racemic and two fully racemic compounds.

The ten isomeric substances formed have been investigated, and, in spite of the facility with which the partly racemic compounds are produced, externally compensated tetrahydroquinaldine can be resolved by means of its condensation products with *d*-oxymethylenecamphor. The method of resolution is based on the fact that *d*-tetrahydroquinaldine condenses much less rapidly than *l*-tetrahydroquinaldine with *d*-oxymethylenecamphor.

220. "*Isomerism of the Oximes.* Part I. *The Diphenylcarbamyloximes.*" By Oscar Lisle Brady and Frederick Percy Dunn. (*Trans.*, 1913, 1613).

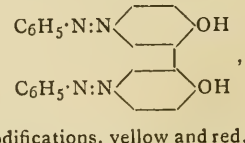
A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1911, xxvii., 239).

221. "*Isomerism of the Oximes.* Part II. *The Nitrobenzaldoximes.*" By Oscar Lisle Brady and Frederick Percy Dunn. (*Trans.*, 1913, 1619).

The authors have investigated the action of sunlight on the nitrobenz*anti*aldoximes, and have shown that in all cases they are converted into the corresponding *syn*-oximes. Hence Ciamician and Silber's statement that the meta-compound does not undergo this change is incorrect. It has also been shown that the *O*-methyl ethers of the nitrobenz*anti*aldoximes are transformed into the *syn*-derivatives by the action of sunlight, but not so readily as are the oximes themselves. Experiments have also been made on the stability of the nitrobenz*syn*aldoximes.

222. "*The Azo-derivatives of* 2 : 2′-*Diphenol.*" By Philip Wilfrrd Robertson and Oscar Lisle Brady. (*Trans.*, 1913, 1479).

5 : 5′-*Bisbenzeneazo*-2 : 2′-*dlphenol*,—



exists in two modifications, yellow and red, both containing half a molecule of water of crystallisation, which is lost only at 160°, the colour of the compounds being unchanged after dehydration.

Several other derivatives have been obtained by the action of 2 : 2′-diphenol on various diazonium salts, although only the simple benzeneazo-compound has been found to exist in two forms. It has been noticed, however, that these compounds almost invariably separate with water of crystallisation, which is retained with unusual persistency, being driven off but slowly at 160°.

223. "*Constitution of the Trinitro*-p-*aminophenols and Trinitro*-p-*anisidines.*" By Raphael Meldola and Frédéric Reverdin. (*Trans.*, 1913, 1484).

The trinitroacetylaminophenol described in 1906 (*Trans.*, lxxxix., 1935) is the 2 : 3 : 6-trinitro- and not the 2 : 3 : 5-trinitro-compound, as appeared from the evidence formerly available. The trinitro-*p*-anisidine melting at 127—128°

(*Arch. Sci. phys. nat.*, 1909, [4], xxvii., 383) has now been proved by direct evidence to be the 2 : 3 : 5-trinitro-compound, and the trinitroanisidine melting at 138—139° (*Trans.*, 1910, xcvii., 444) the 2 : 3 : 6-trinitro-compound. The position of the "mobile" nitro-group in the different series has been shown to be as formerly determined, namely, the 3-nitro-group in the 2 : 3 : 6-series, and in the 2 : 3 : 5-series the 2-nitro-group under the influence of bases, sodium acetate, &c., or the 3-nitro-group on diazotisation of the 4-amino group (*Trans.*, 1910, xcvii., 1204).

224. "*New Method for the Determination of the Concentration of Hydroxyl Ions.*" By Francis Francis and Frank Henry Geake. (*Trans.*, 1913, 1722).

The decomposition of nitrosotriacetonamine into phorone, water, and nitrogen, under the influence of various bases has been fully investigated, the course of the reaction being followed by observing the volume of nitrogen evolved.

The rate of the reaction is proportional to the concentration of the hydroxyl ions, and the results show that, up to a concentration of 0·05N- and beyond 0·3N-hydroxyl ion, a new method has been found for the determination of the concentration of such ions. The utility of this method is indicated by the fact that the effect of neutral salts in moderate concentration on the course of the reaction appears to be negligible.

225. "*Relation between Residual Affinity and Chemical Constitution.* Part IV. *Some Open-chain Compounds.*" By Hans Thacher Clarke. (*Trans.*, 1913, 1689).

Some measurements have been made of the reactivity of tertiary amines of the general formulæ $Me_2N\cdot[CH_2]_n\cdot NMe_2$ and $MeO\cdot[CH_2]_n\cdot NMe_2$ towards ethyl bromoacetate under standard conditions. It was found that the reactive power of the members of both series increases with increasing length of chain; furthermore, in both cases exaltation of reactivity was observed when the atoms of nitrogen and oxygen were situated in the critical positions ($n = 3$ and 4). These results then tend to confirm the hypothesis of "spacial conjugation" in open-chain compounds. In two control series of the general formulæ $CHMe_2\cdot[CH_2]_n\cdot NMe_2$ and $Et\cdot[CH_2]_n\cdot NMe_2$, only slight variations of reactive capacity were observed in the different members.

226. "*Reduction of Mercuric Chloride by Sodium Formate.*" By Alexander Findlay and Morton James Pryce Davies. (*Trans.*, 1913, 1550).

The reduction of mercuric chloride by sodium formate has been studied kinetically at 40°. From the results it appears that the reaction is a bimolecular one, similarly to the reduction of mercuric chloride by phosphorous acid.

227. "*Volatile Constituents of Coal.*" Part III. By Arthur Herbert Clark and Richard Vernon Wheeler. (*Trans.*, 1913, 1704).

Coal can be separated into two substances, differing widely in their characteristics, by the solvent action, first of pyridine and then of chloroform or benzene. The portion of coal soluble in pyridine appears to consist of the resinous constituents, together with some of the humus substances. The latter are insoluble in chloroform or benzene, whereas the resinous constituents are soluble. A separation can thus be made.

Destructive distillation at different temperatures of the separate portions of a bituminous coal obtained by use of these solvents supports the view already put forward (*Trans.*, 1910, xcvii., 1924; 1911, xcix., 649) that coal is conglomerated of two main types of substances, "hydrogen-yielding" and "paraffin-yielding," the former being the degradation products of the celluloses (humus substances), part of which are insoluble in pyridine, and part soluble in pyridine but insoluble in chloroform; and the latter being the resinous constituents, soluble in both pyridine and chloroform.

In an addendum to the paper [with Claude Bernard Platt] attention is drawn to the results obtained by W. J. Russell (*Proc. Roy. Soc.*, 1908, B, lxxx., 432) when investigating the action of resin and allied substances on a photographic plate in the dark, and it is shown that the several portions into which coal can be separated by the solvents pyridine and chloroform affect a sensitised plate in different manners, the results supporting the conclusions drawn from the results of their destructive distillation.

228. "*Volatile Constituents of Coal.* Part IV. *The Relative Inflammabilities of Coal Dust.*" By Richard Vernon Wheeler. (*Trans.*, 1913, 1715).

If coal be regarded as a conglomerate of two main types of compounds, the one readily yielding inflammable gases and vapours on heating to a comparatively low temperature, the other requiring a higher temperature of more prolonged duration to decompose it freely, it can be understood that variations in the proportions in which these different types exist in different coals should cause corresponding variations in the chemical and physical properties of the coals.

A property, common to all coals, which would appear to depend essentially on the proportion of readily-decomposed constituents present, is their "inflammability" when in the form of dust.

It is shown that for a number of coal dusts tested the relative inflammabilities varied directly with the relative proportions of readily-decomposed constituents in the coals.

NOTICES OF BOOKS.

Industrial Organic Analysis. By Paul S. Arup, B.Sc., A.C.G.I. London: J. and A. Churchill. 1913.

This book is intended for the use of the student who has been through a course of theoretical and practical work in pure chemistry and is ready to apply his knowledge to organic technical analysis. It may also be found of use for analytical chemists, serving as a concise work of reference for them, and teachers can learn from it something regarding the nature of the problems with which the practical man has to cope. The intention has been to describe general rather than special methods and complex manufacturing products are not treated, the author limiting himself to the consideration of such materials as coal, petroleum, oils, fats, dairy products, &c. The detection of preservatives in foods is well treated, and the methods chosen for description are well selected. Short theoretical outlines are given as introductions to each chapter, and references to larger treatises are given in great number.

Ensilage. By D. H. de Burgh. Dublin and London: Maunsel and Company, Ltd. 1913.

The author of this little book has a first-hand knowledge of the economical aspects of feeding cattle, both for milk and for beef, through the winter months, and the fact that he has come through some hard experiences and had a good many failures gives his advice all the more weight. The book contains explicit directions for building a silo, growing forage plants for it, and making ensilage. The feeding power of ensilage is discussed, and the chapter on this subject will give the farmer and the colonist some food for reflection. If the author writes didactically he appears to have the weight of facts and figures behind his statements, and to have considered the problem of profitable farming, both in Ireland and in Canada, from many different points of view.

Anorganisch-chemisches Praktikum. ("Practical Inorganic Chemistry"). By Dr. G. H. Riesenfeld. Third Edition. Leipzig: S. Hirzel. 1913.

Although this book is intended for beginners it contains a very complete course of analytical work and preparations in inorganic chemistry, and will be found quite detailed enough for first year college students. It is characterised by the very precise directions given for the preparations, while the analytical reactions and separations are fully

explained, with all the formulæ and equations involved. Some general theoretical conceptions are discussed in an introductory chapter, and throughout the book the physico-chemical point of view is emphasised. The tables of separations, both for anions and cations, are novel in some respects, and are very clear and good. A departure from the usual procedure is introduced in treating the most important acids first, their reactions and separations being regarded as easier for the beginner to study than those of the bases.

Eine Anleitung zur Ausführung exakter Physiko-chemischer Messungen bei Höheren Temperaturen. ("An Introduction to Methods of taking exact Physico-chemical Measurements at High Temperatures"). By Dr. F. M. Jaeger. Groningen: J. B. Wolters. 1913.

ALTHOUGH this book is intended primarily to give workers in the author's laboratory an insight into the methods adopted in high temperature research work, and to enable them to be as independent as possible of personal assistance from demonstrators when they first take up their work, it will give any investigator in the same region an excellent review of such work, for it contains very detailed and clear accounts of the most carefully tested and reliable methods of research, especially those which have been worked out by the author and in the geophysical laboratory at Washington. The author believes that faulty methods are to be blamed for the conflicting data which have been accumulated, and he urges the necessity for the employment of trustworthy standard methods only. The determination of high temperatures is first discussed, and then full details are given of the process of determining the temperature of equilibrium, and the optical and thermic data which can be used in the investigation of silicates are tabulated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances des l'Academie des Sciences. Vol. clvii., No. 12, September 22; No. 13, September 29; No. 14, October 6, 1913.

These numbers contains no chemical matter.

No. 15, October 13, 1913.

Photo-electric Effect of Metallic Compounds.—B. A. Dima.—The photo-electric effect of analogous compounds of the same metal depends upon the valency of the metal in the compound; the higher the valency the smaller the photo-electric power. It is known that the photo-electric effect diminishes more or less quickly as the duration of exposure is increased. In the case of oxides of the same metal, since the lower oxide has the greater tendency to oxidise, and oxidation corresponds to an increase of valency, the lower oxide ought to exhibit fatigue more strongly to the higher, and this is found to be the case. In the halogen compounds of different metals the effect increases with the atomic weight of the halogen (cadmium is an exception). Potassium chloride and lead iodide and bromide become fatigued as quickly in the light as in the darkness. In the case of potassium bromide the photo-electric effect increases very rapidly in the light and diminishes in darkness, finally returning practically to its initial value. With silver bromide and iodide the same phenomenon is observed, except that the effect is always greater than the initial effect. With silver chloride the effect diminishes after small intervals, both in the light and in the dark.

Leucobases and Dyes of Diphenylethylene.—P. Lemoult.—The gentle oxidation of tetramethyldiamido-diphenylcyclohexylidene methane gives a dye the base of which has the formula $C_{23}H_{30}N_2O$; it fuses at 145°, and readily loses water to give the compound $C_{23}H_{28}N_2$. It corresponds to a dye, the formula of which may be written $C_6H_5(H_4)-C<^{OH}_{(Dm)_2}$; *i.e.*, it is tetrahydrogenated malachite green. The presence of the four supplementary atoms of hydrogen considerably modifies the absorbent powers of the solutions for white light.

Atti della Reale Accademia dei Lincei. Vol. xxii. [ii.], No. 4, 1913.

Structure of 3-Nitroso-2-phenyl-indol.—Luigi Alessandri.—The author has prepared 3-nitroso-2-phenyl indol already described by Angeli, and has confirmed his statement that its melting-point is 42°. When ketoximes are heated they undergo the following decomposition:— $3\ ^{R}_{R'}>C-NOH = 3\ ^{R}_{R'}>CO + N_2 + NH_3$. Nitrosophenyl-indol does not give this reaction, but yields a solid isomer melting at 156°. This is a benzoyl derivative formed by the opening of the pyrrol ring, and is isomeric with Pinnow and Sämann's benzoyl derivative. Beckmann's reaction, characteristic of ketoximes, gives positive results when applied to nitrosophenyl-indol.

Formation of Complexes by Alcoholic Hydroxyls.—G. Calcagni.—Glycollic and lactic acids give with iron salts which have the same formulæ as the corresponding salts of chromium, *e.g.*,—

$$\left[Fe_3\ ^{(CH_2OHCOO)_6}_{(OH)_2}\right] CH_2OH.COO.Fe(OH)_3.$$

Benzoic and salicylic acids, on the other hand, in the experimental conditions employed by the author, give only simple compounds of iron and chromium, *e.g.*, $Cr(C_6H_4<^{OH}_{COO})_2$.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 1st.—Royal Institution, 5. General Meeting.
—— Society of Chemical Industry, 8. "Use of Antiseptics for Soil Sterilisation Purposes," by Dr. E. J. Russell and Mr. Buddin.
—— Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof E. G. Coker, D.Sc.
—— Chadwick Public Lectures, 8.15. (At the Institution of Civil Engineers, Great George Street, Westminster). "House Drainage Law," by W. Addington Willis, LL.B.

WEDNESDAY, 3rd.—Royal Society of Arts, 8. "Perfumery," by J. C. Umney.
—— Society of Public Analysts, 8. "Sulphuretted Hydrogen from Artificial Graphite," by W. H. Woodcock and B. Blount. "Determination of Strychnine in the presence of Quinine," by C. Simmonds. "Rate of Liberation of Hydrocyanic Acid from Linseed," by S Hoare Collins and H. Blair. "Composition of Palm-kernel Oil," by G Davidson Elsdon.

THURSDAY, 4th.—Chemical Society, 8.30. "Action of Sulphuric Acid on Copper," by (the late) J. T. Cundall. "Reactions which Occur when Glycerol and Oxalic Acid are Heated together whereby Formic Acid and Allyl Alcohol are Produced," by F. D. Chattaway. "Rotatory Dispersive Power of Organic Compounds—Part V., A Comparison of the Optical and Magnetic Rotatory Dispersions in some Optically-active Liquids," by T. M. Lowry, R. H. Pickard, and J. Kenyon. "Organic Derivatives of Silicon—Part XX, Some Condensation Product of Dibenzylsilicanediol," by R. Robison and F. S. Kipping. "Relation between Chemical Constitution and Depth of Colour of Dyes," by E. R. Watson. "Dyes Derived from Quercetin," by E. R. Watson and K. B. Sen. "Improved Form of Apparatus, based on the Landsberger-Sakurai Process, for the Determination of Molecular Weight," by W. E. S. Turner and C. T Pollard. "Rotation of Optically Active Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts," by G. W. Clough.

Literary Intelligence.—Messrs. Longmans, Green, and Co. have in preparation "Chemistry of the Radio-elements Part II. The Radio-elements and the Periodic Law," by Frederick Soddy, F.R.S. This is an extension of the original monograph and covers recent generalisations connecting the radio-active disintegration series with Mendeleeff's Table.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2819.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

(Continued from p. 261).

WHEN we summarise the results of Treadwell and Escher we find that in solutions of nickel sulphate and ferrous sulphate, which further contain zinc sulphate, the electrolysis at ordinary temperature yields deposits consisting predominantly of zinc. When the electrolysis is performed at higher temperatures, it is possible under suitable conditions of low current density to obtain also deposits poor in zinc. These latter deposits are realised at low current efficiency and at potentials which would likewise be recorded in depositing pure iron or pure nickel from the same solution not containing any zinc; the formation of the former deposits takes place at considerably higher current efficiency, at the potential necessary for the deposition of zinc.

The explanation of these phenomena may first be given with regard to higher temperatures: at small current density the metals nickel and iron are deposited on the cathode at the potential required for their deposition from pure solutions; at the same time that amount of zinc must be deposited which corresponds to the concentration of the zinc ions at the cathode and to the cathode potential. This amount is in itself very small; since, however, both iron and nickel can absorb a good deal of zinc with formation of alloys, considerable amounts of zinc will have to be deposited in order to get into equilibrium as regards cathode potential and concentration of zinc ions. In this way an alloy poor in zinc is formed at the potential of the more noble metal, and the further deposition of iron or nickel on this alloy is effectually retarded. Consequently the hydrogen liberation will predominate. When now the current density is raised, the concentration of the hydrogen ions in the weakly acid solution will no longer satisfy the current, and polarisation is set up; thus the zinc potential is attained. The hydrogen liberation then diminishes, and zinc is chiefly deposited in addition to some more iron and nickel.

At ordinary temperature the separation of nickel and iron even from their pure solutions is much more difficult than at higher temperature (compare A. Schweitzer, *loc. cit.*, and F. Foerster, *loc. cit.*). The retardation of their deposition from the solutions mixed with zinc sulphate will hence be so great from the very first, that only alloys rich in zinc will result at the zinc potential. Thus the experiments described offer the interesting phenomenon that the cathodic passivity of iron and nickel is so much strengthened by the original co-precipitation of zinc, that the deposition of these metals almost ceases and that, at a potential which is by 0·2 volt less noble than that required for the deposition of pure iron and nickel, a cathode deposit will be formed which will essentially consist of zinc. The intensity of this polarisation apparently depends also on the concentration of the hydrogen ions in the electrolyte, because Escher has proved that the rapid rise in the potential takes place with greater difficulty in neutral than in weakly acid solutions. The acidity of the electrolyte hence acts in the sense of an increase in the zinc concentration, *i.e.*, it intensifies the polarisation.

This fact induced us to compare the polarising effect of zinc with the phenomena which accompany the deposition of iron, cobalt, and nickel from the acid solutions of their simple salts. According to F. Foerster's experiments on iron (*loc. cit.*), those of Schildbach on cobalt (*loc. cit.*), and of M. Schade on nickel ("Dissertation," Dresden, 1912), the deposition potential is in these reactions strongly influenced by the concentration of the hydrogen ions in the electrolyte, the effect being such that increased acidity leads to a higher polarisation, other conditions being equal.

The question now arises, how can we account for the polarisation phenomena accompanying the deposition of the iron metals which, as we have seen, are intensified by the presence of zinc sulphate or of hydrogen ions. Le Blanc has expressed the opinion that the metals form ionic hydrates, whose existence is also assumed for other reasons, and that the supplementary supply of metallic ions (for the deposition of the metal) from these hydrates takes place at a restricted velocity only. On this view the moderate velocity of the reaction—

$$Me_n(H_2O)++ \rightleftharpoons Me_n++ + H_2O$$

in the direction left to right would be the cause of the high polarisation in the deposition of the metals, and the increase in the polarisation, observed in the presence of zinc sulphate or acid, would occur because these additions much retard the decomposition of the ionic hydrates. Such an inhibitory action is possible; it appears little plausible, however. It seems preferable to look for the cause of the retardation of the cathodic reaction in some change of the cathode surface. We may suppose that alloys containing zinc or hydrogen are deposited on the cathode, and they possess a higher electrolytic solution pressure than the pure nickel or iron. The formation of the—for the present purely hypothetical—intermediate products would then be the cause of the marked retardation in the deposition of the metals.

The experiments which have been mentioned clearly demonstrate, at any rate, that a retarded cathodic process may undergo a further pronounced retardation when the cathode takes up foreign matter. If that be granted, the assumption which is made in explanation of the anodic passivity, namely, that slowly-proceeding anodic reactions are further and essentially retarded by the formation of oxygen alloys in the surface of the anode, gains a higher degree of probability. In addition to this passivity which is due to an oxygen charge, there will also be a possibility of passivity during the anodic dissolution of metals in cases where the cations emitted by the anode will be able to form a scarcely soluble compound with the anions of the electrolyte. We shall only then be justified in ascribing the passivity to surface films if such films may be expected to form in accordance with the chemical behaviour of the electrolyte near the anode. When the causes of the anodic passivity are discussed, the question will therefore not be quite general, whether any retardation in the emission of the ions may arise from the formation of an oxygen alloy on the surface of the anode, or whether the retardation be caused by the mechanical closure (covering up) of the surface of the electrode by the formation of an oxide skin or of some other scarcely soluble precipitate. According to the conditions of the experiment, the one or the other moment will cause passivity.

I now wish to refer to some experiments of mine (*Zeit. Elektrochem.*, 1912, xviii., 189) which show that, at one and the same electrode metal in the same electrolyte, there may, according to the experimental conditions, be a passivity of the surface films, as well as a passivity due to an oxygen charge, and that, under suitable conditions, the two phenomena may continuously pass into one another. The experiments were undertaken, in the first instance, for the purpose of inquiring into the suitability of various metals as electrodes for the electrolytic preparation of ferripotassium cyanide. I determined current density-potential curves with anodes of the several metals in

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12 1913.

neutral and in alkaline solutions containing both ferro- and ferripotassium cyanide. The sheet metals were dipped into the electrolyte; the potential was measured first without current; the electrode was then anodically polarised while the electrolyte was well stirred, and the current density was raised, and the potential was determined in the usual way.

We are on this occasion interested only in the results obtained with the metals platinum, gold, iron, nickel, cobalt, and copper. The polarisation phenomena varied to an extraordinary degree with the experimental conditions. When the electrolyte was a neutral solution with a total content (of ferropotassium cyanide + ferripotassium cyanide) of 0·5 mol., whilst the ratio $K_4FeCy_6 : K_3FeCy_6$ in the solution was 25 : 75 or 75 : 25, the potential found, when the current was not flowing, with platinum and gold electrodes was the oxidation potential of the respective solution, whilst much less noble potentials were observed with iron, cobalt, nickel, and copper; these latter potentials gradually became more noble, however. The latter electrodes at the same time became covered with films of their sparely soluble ferrocyanogen compounds. Thus gold and platinum were completely passive in neutral solutions, whilst iron, nickel, cobalt, and copper behaved at first like soluble electrodes which gradually became covered with surface films and assumed the nobler, passive potential. When the electrodes were now anodically polarised, gold and platinum too showed the

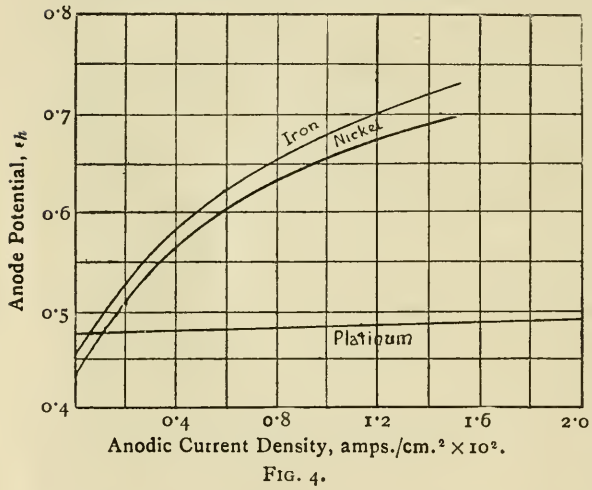


FIG. 4.

small polarisation (due to changes in concentration), whilst an extraordinarily intense polarisation was noticed on the other electrodes, which were covered with surface films. The current density-potential curves observed with iron, nickel, and platinum in neutral solutions are reproduced in Fig. 4. We see how very strong the polarisations are in the first two cases (anodes with surface films) compared with the concentration polarisation of the platinum anode.

The aspect changed very materially when the same solution of ferro- and ferricyanide was rendered 0·1 N alkaline by the addition of KOH. In this solution not only gold and platinum but also iron, cobalt, nickel, and copper marked, when not under current, the oxidation potential of the electrolyte; the appearance of a surface film was no longer noticeable in any case; all the metals remained perfectly bright. When the electrodes were anodically polarised in this instance, the same small concentration polarisation was shown by all the metals except iron. Iron yet indicated in the alkaline solution a pronounced polarisation which could considerably be dimnished, it is true, by increasing the alkalinity of the electrolyte and by raising the temperature, but which could never be reduced to the low values measured at the other metals. In these experiments, however, the eye could not discern the formation of any surface film on the iron. But the film was visible when the experiment was made in a 0·01 N alkaline solution. In this solution the iron electrode marked, a short while after immersion, a potential which was by 8 millivolts less noble than the oxidation potential of the solution. Within half an hour, however, the iron potential had risen to this value, while the electrode became covered with a faintly discernible layer of Prussian blue, which was gradually decomposed by the alkali of the electrolyte and converted into an oxide film. This oxide film could only be seen in some spots; the rest of the surface appeared quite bright. Under anodic current this electrode gave a still higher polarisation than had been noticed in the 0·1 N alkaline solution. The existence of an invisible oxide film had, however, to be presumed also in more strongly alkaline solutions, since the polarisation was gradually seen to increase in them when the current intensity was kept constant and the electrolyte remained unchanged. Thus in a 0·1 N alkaline solution, *e.g.*, the polarisation rose, at 0·002 amp./cm.², in 265 minutes from 90 up to 134 millivolts. These observations indicate that in all probability the passivity of the iron electrode in alkaline ferro-ferricyanide solutions was also due to the formation of an oxide film.

On the contrary, the passivity of electrodes which showed merely concentration-polarisation in alkaline solutions could not be attributed to an oxide film of similar kind as with the iron electrode. This was concluded, in the first instance, from the non-observance of any increasing polarisation, and further from the following experiments:—

When by suitable previous treatment a very thin translucid oxide film had been produced on electrodes of nickel or cobalt, these electrodes showed, in alkaline ferro-ferricyanide solutions, at once the same polarisation phenomena of the same order of magnitude as iron electrodes. If, therefore, the passivity had on nickel, cobalt, and the other metals which were not polarisable in alkaline electrolytes, been caused by the same kind of oxide layers, this passivity should have called forth an intensified polarisation. As this was not the case, we should have been forced—provided we declined to abandon the surface layer as cause of the polarisation—to assume that these surface films responsible for the passivity were good conductors, capable indeed of impeding the emission of cations, but not of opposing any resistance to the passage of the current. The existence of such well-conducting films is, however, extremely improbable, since the oxide skins formed by purely chemical means introduced a considerable polarisation.

If, in spite of that, it should be suggested that the passivity films were of the same kind as those chemically prepared, but of so insignificant a thickness that they could not give rise to any pronounced polarisation, we should have to imagine that the oxidations of ferrocyanide were taking place under the co-operation of some peroxide in the oxide layer. We could not conceive then, however, why such peroxides, whose existence we should have to assume for the different metals gold, platinum, nickel, cobalt, and copper in alkaline solutions, should all be able to effect the oxidation of the ferrocyanide at the same potential and with the same velocity. On account of this equality of the potential, at which the oxidation of the ferro-ferricyanide solutions is taking place with different metals, we shall have to suppose that there is no oxide film on these metals (which cannot anodically be polarised), but that these metallic surfaces are in perfect contact with the electrolyte. Since therefore the presumption of oxide films does not afford any unstrained explanation of the cause of the passivity of platinum, gold, nickel, cobalt, and copper, it appears apposite to trace their passivity back to a retardation in the emission of cations consequent upon the charge of the anode with oxygen.

Such oxygen charges must doubtless exist, to judge

from the position of the potentials of the anodes in the anodic oxidation of ferro ferripotassium cyanide solutions. We must further suppose these charges to be stronger in alkaline than in neutral solutions, since they must be in equilibrium with the concentration of the hydroxyl ions in the electrolyte. The last-mentioned fact was proved by Fredenhagen (*Zeit. Anorgan. Chem.*, xxix., 396) by comparing the potentials of alkaline ferro ferripotassium cyanide solutions with the potentials of oxygen electrodes in alkali solutions of equal concentrations. It resulted that the former potentials were more noble than the latter (oxygen) potentials, and that this potential difference increased with increasing alkali concentration of the electro lyte. That shows that the oxygen pressure acting upon an electrode immersed in an alkaline ferro-ferricyanide solution is likewise increased by the higher alkaline concentration of the electrolyte. The pressure is materially smaller in a neutral ferro-ferricyanide solution than in an alkaline solution. Thus it comes about that nickel, cobalt, and copper are still able to emit cations into the electrolyte in neutral ferro-ferricyanide solutions, but that the rate of ion formation has practically dwindled to zero in alkaline solutions, owing to the increased oxygen charge. In the case of iron the rate at which ions can be formed is likewise much diminished in alkaline solutions. It is yet sufficient though to cause the formation of oxide films. The passivity phenomena of the experiments described mainly depend upon the special position of the ferro-ferripotassium cyanide potential, and it is entirely within the range of possibility that, at more noble potentials, the metals examined would show a very different behaviour.

The question in which way the oxygen charge of the anode impedes the emission of cations from the anode cannot yet be answered. If we assume with O. Sackur (*Zeit. Elektrochem.*, 1904, x., 841), as well as with F. Haber and J. Zawadsky (*Zeit. Physik. Chem.*, 1911, lxxviii., 228), that the primary process of the anodic polarisation of a metallic electrode signifies in every case, and therefore also in the case of a soluble anode, the discharge of the anions, then the passivity phenomena which we have been discussing would have to be considered from the same point of view as the retardation of the discharge of halogen ions from platinum electrodes. It has long been recognised (compare E. Müller, *Zeit. Elektro-Chem.*, 1900, vi., 573; 1901, vii., 750; 1902, viii., 424; Luther and Brislee, *Zeit. Phys. Chem.*, 1903, xlv., 216; Böricke, *Zeit. Elektrochem.*, 1905, xi., 71; Pfleiderer, *Zeit. Phys. Chem.*, 1909, xlix.), that, especially with smooth platinum, the discharge of the halogens from solutions of the halides takes place at potentials which are materially more noble than we should expect from the position of the equilibrium potentials of the halogens in the respective solutions.

(To be continued).

The Physical Society's Annual Exhibition.—This Exhibition, which is to be held on Tuesday, the 16th inst., at the Imperial College of Science, South Kensington, will be open in both the afternoon (from 3 to 6 p.m.) and in the evening ((from 7 to 10 p.m.). Prof. The Hon. R. J. Strutt, F.R.S., will give a Discourse at 4.30 on "Spiral Electric Discharges"; and Mr. Louis Brennan, C.B., will show some experiments with Soap Films at 8.30 p.m. Some thirty firms will be exhibiting, and there will also be certain experimental demonstrations. We understand that invitations have been given to the Institution of Electrical Engineers, the Institution of Mechanical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore Members of the Societies just mentioned (including also the Physical Society) desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

I. *Introduction.*

1. *The Properties of Liquid Ammonia.*—The many striking analogies between liquid ammonia and water as electrolytic solvents have been emphasised by the writer and his co-workers in papers which have appeared from time to time during the past decade. In all those properties which give to water its unique position among solvents, such as its abnormally high boiling-point, its high specific heat, its high heat of volatilisation, its high critical temperature and pressure, its high association constant, its high dielectric constant, and its low boiling-point elevation constant, its power as an electrolytic solvent, and the facility with which it forms compounds with salts, liquid ammonia shows a remarkable similarity to water.

While the boiling-point of liquid ammonia is 33·46° below zero (Gibbs, *Journ. Am. Chem. Soc.*, 1905, xxvii., 851; *cf.*, Franklin, *Ann. Phys.*, 1907, [4], xxiv., 367), it still appears abnormally high when compared with the boiling temperatures of phosphine, arsine, stibine, methane, ethylene, hydrogen sulphide, hydrochloric acid, &c. The specific heat of liquid ammonia (Elleau and Ennis, *Journ. Frank. Inst.*, 1898, cxlv., 189; Dieterici, *Zeit. Kälteind*, 1904) and the heat of fusion (Fourcrand and Massol, *Comptes Rendus*, 1902, cxxxiv., 653, 743) of the solid are greater than the corresponding constants for water or any other known substance, while its heat of volatilisation (Elleau and Ennis, *loc. cit.*; Franklin and Kraus, *Journ. Phys. Chem.*, 1907, xi., 553; Dieterici, *loc. cit.*) with the one exception of water, is the highest of any known liquid. The critical temperature of ammonia is abnormally high, and its critical pressure—the more characteristic constant—is higher than that of any other liquid excepting water. Ammonia is an associated liquid (Franklin and Kraus, *Am. Chem. Journ.*, 1899, xxi., 14; Walden, *Zeit. Phys. Chem.*, 1911, lxx., 599), and its dielectric constant (Goodwin and Thomson, *Phys. Rev.*, 1899, viii., 38; Coolidge, *Wied. Ann.*, 1899, lxix., 125), though much below that of water, is still high when compared with that of non-electrolytic solvents. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3·4 (Franklin and Kraus, *Am. Chem. Journ.*, 1898, xx., 836), as compared with 5·2 for water. In its tendency to unite with salts and other compounds, it probably exceeds water, since salts with ammonia of crystallisation are perhaps even more numerously recorded in the literature than are salts with water of crystallisation. As a solvent for salts it is generally much inferior to water (Franklin and Kraus, *Ibid.*, 1898, xx., 820), though some salts, for example the iodides and bromides of mercury, lead, and silver, dissolve very much more abundantly in ammonia than they do in water, and it far surpasses the latter solvent in its ability to dissolve the compounds of carbon. Finally, it exhibits conspicuous power as an ionising solvent (Note 1), the more dilute ammonia solutions at 33·5° being very much better conductors of electricity than aqueous solutions of the same concentration at 18°.

II. *Metathetic Reactions between Ordinary Acids, Bases, and Salts in Liquid Ammonia Solutions.*

2. *Reactions between Salts.*—The general resemblance between ammonia and water, outlined above, led Franklin and Kraus to inquire whether ordinary metathetic reactions take place in the former solvent as they do in the latter. Such was found to be the case (*Am. Chem. Journ.*, 1899, xxi., 1), with the interesting difference that, as a result of variations in the order of solubilities in ammonia as compared with water, certain reactions take place in the former solvent which do not occur in the latter, or they

* From *American Chemical Journal*, xlvii., No. 4.

may even proceed in opposite directions in the two solvents. As examples may be mentioned the separation of the sulphides of the alkaline earths as white precipitates when liquid ammonia solutions of soluble salts of these metals and ammonium sulphide are brought together, and the precipitation of an alkaline earth chloride when a solution of a soluble salt of any one of these metals is acted upon by a solution of a soluble chloride. The equation $2AgNO_3 + BaCl_2 = Ba(NO_3)_2 + 2AgCl$ read from left to right, represents the familiar action between silver nitrate and barium chloride in aqueous solution. Read from right to left it represents the action of silver chloride on barium nitrate in solution in liquid ammonia. Barium chloride is but slightly soluble in liquid ammonia, while the other three salts are readily soluble.

3. *Reactions between Acids and Bases.*—At first thought it may seem absurd to speak of acids existing in ammonia solutions and reacting therein with bases. Ammonia is frequently referred to as a base, and every one knows that acids unite with ammonia to form the familiar ammonium salts. The fact, however, is to be emphasised that ammonia is not a base, that it is only in the presence of water that ammonia exhibits basic properties, and that in consequence the dry liquid behaves almost, if not quite, as indifferently as water itself towards the ordinary indicators. Now it is an important fact that many ammonium salts of both oxygen acids and halogen acids dissolve freely in the liquid ammonia to form solutions which show certain truly acid properties, as follows:—First, they discharge the red colour of liquid ammonia solutions of phenolphthalein which have been rendered alkaline by the addition of a small quantity of a base; second, solutions of ammonium salts in ammonia attack sodium, potassium, calcium, magnesium, zinc, and cadmium, with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation $M + NH_4Ac = MAc + NH_3 + H$; third, many metallic oxides and certain basic salts—all the members of which two classes of compounds are practically insoluble in ammonia—dissolve in liquid ammonia solutions of ammonium salts. For example, Divers (*Phil. Trans.*, 1873, clxiii., 359) found sodium hydroxide, potassium hydroxide, and the oxides of cobalt, copper, lead, magnesium, mercury, cadmium, and zinc to be soluble in liquid ammonia solutions of ammonium nitrate (Note 2). The writer has confirmed most of these results of Divers, and has also observed the solubility of some of these hydroxides and oxides in solutions of ammonium salts other than the nitrate. It therefore appears that bases dissolve in ammonia solutions of ammonium salts (Note 3) in a manner analogous to the solution of insoluble bases in aqueous acid solutions, as indicated, for example, by the familiar equations—

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$

$$Ca(OH)_2 + 2NH_4NO_3 = Ca(NO_3)_2 + 2H_2O + 2NH_3$$

for two of the above mentioned bases.

Even in water solutions the acid properties of ammonium salts are frequently in evidence, as, for example, in the well known cases of the solubility of metallic zinc and magnesium, and of certain metallic oxides, hydroxides, and carbonates, in aqueous solutions of ammonium salts. Especially interesting and significant in this connection, as will be discussed in detail in a subsequent paper, is the conversion of the so-called mercuriammonium compounds into normal mercuric salts by the action of ammonium salts in aqueous solutions.

The reactions which have just been described as taking place in liquid ammonia differ in no essential respects from the familiar metathetic reactions in aqueous solutions. They are reactions between the ordinary oxygen acids, bases, and salts and the halogen acids and salts, taking place in a solvent other than water, a field of study that has received considerable attention from Neumann and his students (*Ber.*, 1910, xliii., 313; Rohland, *Zeit. Anorg. Chem.*, 1898, xviii., 322).

Notes.

1. Cady, *Journ. Phys. Chem.*, 1897, i., 707; Franklin and Kraus, *Am. Chem. Journ.*, 1900, xxiii., 277; Franklin and Cady, *Journ. Am. Chem. Soc.*, 1904, xxvi., 499; Franklin and Kraus, *Ibid.*, 1905, xxvii., 191; Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 272.

It will be observed that it is the hydrides of the first or typical members of the fifth and sixth groups of the Periodic System which show conspicuous power as electrolytic solvents. The hydrides of the other members of these groups (hydrogen sulphide, phosphorus hydride, &c.) show scarcely a trace of such properties. Of the members of the seventh group, Steele, Archibald, and MacIntosh have shown that hydrochloric acid, hydrobromic acid, and hydriodic acid show some considerable power of forming electrolytic solutions. Such relationships, together with the fact that the discovery of fluorine was made possible to Moissan by the observation that potassium fluoride dissolves in liquid hydrofluoric acid to form a conducting solution, suggests that hydrofluoric acid may be as powerful, or possibly even more powerful an ionising agent than water itself. Some of these considerations, together with the facts of its abnormally high boiling-point, its evident association even in the gaseous state, its power of uniting with fluorides as hydrofluoric acid of crystallisation, led the writer, some years ago, to make some preliminary experiments on liquid hydrofluoric acid in the hope that he might see his way to a more extended investigation of liquid hydrofluoric acid as an electrolytic solvent. These preliminary experiments on anhydrous hydrofluoric acid showed it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, sodium nitrate, sodium chlorate, potassium bromate, acetamide, urea, and potassium sulphate, are abundantly soluble; silver cyanide, barium fluoride, and copper chloride appear to dissolve to some extent; while calcium fluoride, copper sulphate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride, and metallic magnesium, are insoluble.

2. The so-called Divers liquid, it is to be observed, is simply a concentrated solution of ammonium nitrate in liquid ammonia. The fact that the solution exists at ordinary temperatures at atmospheric pressure is explained as the result of the lowering of the vapour tension of the solvent by the large amount of ammonium nitrate in solution (Kuriloff, *Zeit. Phys. Chem.*, 1898, xxv., 108; Divers, *Ibid.*, 1898, xxvi., 430).

3. The acid properties of ammonium salts in liquid ammonia solutions thus made evident suggest that, analogously, in water solutions of hydrochloric acid the hydrogen ion may be associated with water as OH_3^+. Three hydrates of hydrochloric acid of the respective formulæ $HCl.3H_2O$, $HCl.2H_2O$, and $HCl.H_2O$ are known (Rupert, *Journ. Am. Chem. Soc.*, xxxi., 851). Of the latter compound it is interesting to note that Rupert reports it as a "white crystalline substance resembling ammonium chloride in general character."

(To be continued).

Fluorsulphonic Acid and its Salts.—Wilhelm Traube.—Ammonium fluoride reacts energetically with sulphur trioxide, giving a crystalline product, the ammonium salt of fluorsulphonic acid, FSO_3NH_4. The same salt may be obtained by dissolving ammonium fluoride in fuming sulphuric acid, and the free acid may be obtained by distilling the solution. On treating the solution with alcoholic ammonia and evaporating off the alcohol, ammonium fluorsulphonate is formed, and fluorsulphonates are also obtained when dry fluorides are heated with pyrosulphates. They are decomposed by heating with alkalis, but the acid is much more stable towards hydrolysing agents than the analogous chlorsulphonic acid. When salts of fluorsulphonic acid are heated with 99 per cent sulphuric acid in a platinum dish fitted with an upright platinum condenser a good yield of the free acid is obtained.—*Berichte*, xlvi., No. 12.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A New Lamp for Ultra-Violet Rays.

MM. Billon-Daguerre, Niedard, and Fontaine have just invented a new mercury vapour lamp which acts completely immersed in water and can only work in water. The light, rich in ultra-violet rays, emitted by this lamp does not heat the objects placed near the luminous source. This particular would permit an inflammable film to remain indefinitely in proximity with the lamp without taking fire.

Jupiter's White Spot.

The astronomers who study the physical constitution of Jupiter have not yet managed to agree as to the nature of a spot that for a long time went under the name of the "red spot," and which is now white. This mysterious spot has the aspect of an enormous swelling. It occupies an important region of the southern hemisphere of the Jovian planet. The extent of this spot is exceedingly vast. It is about 42,000 kilometres in length. It is very probably formed by gaseous condensations, for the surface of Jupiter is still in a primordial gaseous or liquid state. Contradictory hypotheses have been formed about it. Certain scientists see in this spot of Jupiter a first continent, in formation a thin pellicule that is cooling on the surface of the immense and majestic planet. Other astrophysicists think that this spot is merely constituted by a condensation in the vaporous envelope of Jupiter. An astronomer of the Observatory of Copenhagen, M. Hans Lan, has just published the result of his observations on Jupiter's "red spot." According to this astronomer the visible surface of Jupiter is composed of a vaporous envelope, the gases of which are perhaps very much condensed and form a light yellow layer, with a great power of reflection. Above this is spread a thin layer, which appears to exercise a strong absorption on the under layer. In this very fluid middle formed of clouds and vapours, the spot may be considered, says M. Hans Lan, as a hot lake in the deep layers of the gaseous envelope. The temperature of the spot must be much higher than that of the neighbouring regions. So masses of gas, veritable currents of metals or metalloids fall into it. Its form varies under these influences, but for some years past the red colouring has decreased, the spot has gradually grown pale. It is at present of a brilliant white. The tropical perturbations of the austral hemisphere of Jupiter seem to have an influence on the spot. These perturbations push it from west to east, and M. Quénissel, astronomer at the Flammarion Observatory at Juvisy, has signalled an average advance of about one degree a day. For M. Quénissel the spot is a solidification of the Jovian surface. This is not the opinion of M. Hans Lan. The Danish astronomer states that the disjunction of the spots on Jupiter recalls that of the spots on the sun; their brilliancy varies with the activity of the sun and especially with its magnetic phenomena. These variations of brilliancy have been likewise remarked by M. Fridtjof Le Coultre, an astronomer of Genève. And the gleams that suddenly appear in this reddish region may be attributed either to the lighting up of the Jovian clouds by some volcanic eruption or to some magnetic aurora of extreme intensity. But the problem of the formerly blood red spot of Jupiter is not yet solved. Is it merely clouds or worlds in a state of formation? Doubtless science will tell us some day what it is.

The World's Statistic of Telephone.

An interesting statistic concerning the distribution of telephone throughout the whole world has just been published by the *Lumière Electrique*. The total number of telephonic stations of Europe, Asia, and America was in January, 1912, 12,085,713, whereas on January 1, 1911, there were only 10,919,100 telephones. It was in America that the number of stations increased to such an extent in one year: 760,000 more telephones as compared with an increase of only 200,000 apparatus in Europe. The United States have the greatest number of telephones of any country in the world, with 8,357,625 apparatus, for a population of 92,174,000 inhabitants; that is to say, a telephone post for every 11 inhabitants. Canada follows next with 23 inhabitants per post and a number of 302,759 telephones. Amongst European countries, Denmark holds the first place with 107,153 apparatus for 2,589,000 inhabitants, 1 telephone for every 24 Danes. Sweden and Norway occupy the second and third place. Switzerland comes next with 41 inhabitants per telephonic station. Germany is the fifth with 1,154,518 telephones, or one apparatus for 56 inhabitants. England comes next, followed closely by Luxembourg, Iceland, and Holland. France occupies miserably the tenth place in the European statistic, with 260,998 telephonic posts; that is to say, one apparatus for 150 Frenchmen. The two last ranks are held by Bulgaria, Greece, and Bosnia-Herzegovina, that have only one telephonic apparatus at the disposition of from 1500 to 2000 inhabitants. The ten towns of the whole world that are best provided for as far as is concerned the number of installed telephones are, with the exception of Stockholm, all American. At Los Angeles, at San Francisco, and at Stockholm there is one telephone per $4\frac{1}{4}$ inhabitants, which seems almost incredible, but is in reality rigorously exact.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 20th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*On* Medullosa pusilla." By Dr. D. H. Scott, For.Sec.R.S.

"*Neuro-muscular Structures in the Heart.*" By Prof. A. F. S. Kent.

"*Alleged Excretion of Creatine in Carbohydrate Starvation.*" By George Graham and E. P. Poulton.

1. The presence of aceto-acetic acid always causes an error in the estimation of creatinine, and the error increases with increasing amounts of aceto-acetic acid. As the result of this error the estimation of creatinine will be too low. This error is not eliminated if the diluted urine is allowed to stand for varying lengths of time before making the readings.

2. The aceto-acetic acid is removed in the estimation of creatinine + creatine, and does not cause any error.

3. As the creatinine figure is too low and the creatinine + creatine figure is correct, it will appear that creatine has been excreted.

4. Acetone and oxybutyric acid, if present in amounts comparable to those which usually occur in urine, produce practically no error in the estimation of creatinine.

5. A simple and reliable method has been devised for removing aceto-acetic acid, preliminary to the estimation of creatinine.

6. In our experiments a carbohydrate-free diet did not cause the excretion of any creatine.

"*Origin and Destiny of Cholesterol in the Animal Organism.* Part XI. *The Cholesterol Content of Growing Chickens under different Diets.* By J. A. Gardner and P. E. Lander.

In this paper the authors give an account of determinations of the cholesterol and cholesterol ester content of chickens at various stages of growth and under diets containing different amounts of cholesterol, with a view to ascertaining whether cholesterol can, to any extent, be synthesised in the organism from proteins, fats, or

carbohydrates. The results appear to show that the cholesterol content of the growing chicks depends on the sterol content of the diets, but the figures give no indication that, under the conditions of experiment, cholesterol is synthesised during growth.

The authors consider that the results obtained, taken in conjunction with the fact previously discovered, that in the differentiation of the ovum into the complex aggregates of cells constituting the chick no formation of cholesterol takes place, appear to support the view formerly expressed that cholesterol is not readily synthesised in the organism.

"*Contributions to the Biochemistry of Growth. On the Lipoids of Transplantable Tumours of the Mouse and the Rat.*" By W. E. Bullock and W. Cramer.

Anniversary Dinner, *December 1st*, 1913.

A very large company of eminent men of science was present at the anniversary dinner held in the evening of December 1st at the Hôtel Métropole, at which the new President, Sir William Crookes, O.M., presided. Among those who accepted invitations to be present were :—

The American Ambassador, Sir Archibald Geikie, the Greek Minister, Sir John Simon, Lord Desart, Lord Sumner, Sir Joseph Larmor, M.P., Sir William Ramsay, Sir Aston Webb, Sir Oliver Lodge, Sir E. Ray Lankester, Sir Henry Miers, Sir Francis Younghusband, Sir David Gill, the Hon. Thomas Mackenzie (High Commissioner for New Zealand), the Dean of St. Paul's, the Dean of Westminster, the Vice-Chancellor of Cambridge, Sir Frederic Kenyon, Sir Newton Moore (Agent-General for Western Australia), Sir Thomas Elliott, Sir Frederick Treves, Sir Francis Laking. Sir Ronald Ross, Sir Alfred Kempe, Sir J. Crichton-Browne, Mr. J. H. Balfour Browne, Sir Laurence Gomme, Sir J. Wolfe Barry, Sir Charles Parsons, Sir William Abney, Sir Lauder Brunton, Sir Thomas Barlow, Sir George Robertson, Sir John Murray, Sir Mackenzie Davidson, Sir David Ferrier, Mr. Justice Pickford, Lord Onslow, Sir Alfred Keogh, Sir Thomas Holderness, Sir Alfred Ewing, Sir Reginald Custance, Sir William Tilden, Sir H. Llewellyn Smith, Sir John Bradford, Sir Andrew Noble, Sir John Thornycroft, Sir Edward Troup, Sir Hercules Read, Sir Sydney Olivier. Professor A. Schuster. Sir William Schlich, Sir H. Howarth, the Rev. Dr. Bonney, Dr. A. Smith Woodward, and Professor E. H. Starling.

After the usual loyal Toasts, the American Ambassador, in proposing the toast of "The Royal Society," spoke of the change which had come into the world by reason of the activities that that venerable society had fostered—a change even in our day. Let anyone think, for instance, what it was to live in the pre-Darwinian era as compared with what it was to live in the post-Darwinian era. For his part, he thanked God he was born no earlier than he was. (Laughter). With the rich flowering of science, however, had come a bankruptcy of great literature. He left it to them to say whether these two contemporary phenomena bore the relation of cause and effect. By great literature, of course, he meant not the mere conveying of information, but the great art which used life and thought for its raw materials, and used it with such insight that they called it inspiration, and with such deft artistry that they called it genius. Might not the explanation of this bankruptcy of great literature be that the rise of science, which had changed all our outlook on the world, and had for the first time made us feel at home in this life and unafraid, had for the moment thrown men of great artistic power somewhat out of the use of their powers? It was a pleasing thought to suppose that some member of that society, or some similar body, might make a new era also by the production of great literature, because the great literature of the future must take account of and must be shaped by their view of life under the dispensation of men of science. (Cheers).

The Government and Scientific Problems.

The President said he felt it impossible to express his sense of the distinction they had conferred on him by electing him as their President—the highest reward that could fall to the lot of an English scientific man. The Society's aims are well known to all present, but possibly their needs are not quite so famliiar. They are in the not uncommon position of requiring large annual sums to supplement their comparatively small income, which is entirely devoted to the furtherance of scientific knowledge. They have had generous benefactors in the past, and every year the Government places a certain sum of money at their disposal. But they could advantageously dispense, in aid of investigation, very much larger grants than are now in their gift, and they can promise most enthusiastic gratitude to the fortunate possessor of wealth who is yet to come forward with an offer to double or treble their income.

During the past year they had been consulted by the Government on many scientific problems, and they were gratified by the assurance that their advice had been of practical value. They had appointed a sub-committee to prepare the reports of the scientific work of the Terra Nova Antarctic Expedition, and to administer the sum of £17,500 set aside by the Mansion House Committee for that purpose. The Society had also made an investigation into the cause and prevention of glass workers' cataract, and had appointed a committee to administer the small amount of funds granted by the Government for that purpose. They were also proceeding to revise the main features of the magnetic survey of the British Isles, and had appointed a small committee for that purpose.

From his earliest days the Royal Society exerted on him a stimulating influence. It was in 1850—sixty-three years ago—that he first attended a Meeting in the Society's Rooms at Somerset House. More than fifty years ago he was elected a Fellow, and in November, 1863, he was received into the Society by Sir Edward Sabine, and he signed the noted book of Signatures. On the same page as his own occurred the names of Sir William Huggins, Sir Archibald Geikie, Sir Charles Murchison, David Livingstone, Sir William Flower, Sir William Jenner, Lord Tennyson, and Sir John Evans. He had the extreme honour of being the only chemist– with the exception of Sir Humphry Davy—who had occupied the Presidential Chair. He had watched the development of chemistry from the stages of observation and classification to the deductive stage of the Newtonian method. He saw now with inward eye, how advances in science research depended upon absolute accuracy of observation, measurement, expression, reasoning, and on scrupulous veracity combined with the widest tolerance of new ideas. And he saw the disdain of scientific teaching—which used to be a characteristic of our industrial leaders—slowly and surely vanishing. This disdain had been replaced by a keen belief in pure research.

After referring to modern progress, he said :—"How extraordinary it is that we have not yet realised that conceivability is not the limit of possibility; that the true opposite of belief in a theory or a fact is not disbelief but doubt, uncertainty, suspension of judgment."

"I wonder," continued Sir William, "what parallel of our appalling ignorance our grandchildren will quote in eighty years' time? What obvious phenomena are overlooked, and what inferences and generalisations are awaiting another Newton? The keen sense of failure, the memory of disappointment and of errors must ever accompany the pursuit of knowledge. Despair is close behind us—enough that it never looks us in the face. But it is unnecessary for me to tell you that it is the work itself that comes first; not the reward. No rejoicings in praise or profit rival the joy of sustained effort, patient labour, even if success does not come at the end to crown the toil. But it is the approbation of the Royal Society that is, indeed, my 'exceeding great reward.'"

Sir Joseph Larmor, in proposing the toast of "The Retiring President," referred to the high literary qualities which Sir Archibald Geikie had combined with profound scientific work, and which had brought the Royal Society into honour and appreciation in circles in which perhaps the hard strenuous routine of difficult scientific work might not have been appreciated on its merits alone.

Sir Archibald Geikie, in responding, said it was not merely an honour to have occupied the chair which was filled by Newton, Sir Humphry Davy, Hooker, Huxley, Kelvin, and Lister. It had been to him a source of the most intense enjoyment and also a great revelation of human nature, chiefly on the pleasant side. It was a great pleasure, indeed, to cultivate friendships with such men as Sir Joseph Larmor himself, Sir Alfred Kempe, Sir Rose Bradford, Prof. Schuster, and all the men with whom he had been associated in the Council. He was deeply indebted to the Royal Society. The only regret which he had to express was that the hope with which he entered upon his Presidency had not been realised, that somehow or other by benefactions—he never looked very much to the State for anything (laughter)—by donations, or be quests, the Royal Society would have been in possession of such a sum, apart altogether from its ordinary income and expenditure, as would enable it to carry out, initiate, and support investigation which at present, for want of funds, it was absolutely unable to do. That had been only partially fulfilled. The Society ought to be in possession of a sum of, say, £1000 a year which it could do what it liked with. He was thinking over these matters when Sir James Caird, of Dundee, sent him a cheque for £5000, expressing the hope that it might possibly be of use in cheapening radium, but fortunately coupled it with this stipulation, "or with any other branch of research which the Society might think it useful to devote it to." Sir J. Caird had been so good as to agree that the fund should be named the "James Caird Fund for Physical Research." That was the sort of fund they wanted—a fund which should not be restricted to any one thing. (Cheers).

The President next proposed "The Medallists," whose names were received with cheers by the company. He prefaced his speech with a few personal remarks, in the course of which he said he hardly dared hope to rival his great predecessor, who, by his personal qualities no less than by his intellectual attainments, had won the esteem and affection of all who had come in contact with him. (Cheers).

Sir Ray Lankester, in responding, expressed the thanks of the medallists for the toast which had been honoured. He was very proud to be associated in so doing with the distinguished men to whom medals had that day been awarded. Most of them were his lifelong friends and associates. In the Sylvester Medallist of the year, Dr. Glaisher, he met an old schoolfellow. They were at school together when Colet's School stood near St. Paul's Churchyard. They both owed much to the fact that St. Paul's was an old-fashioned day school where they were little troubled with evening work and had leisure to follow their favourite studies at home. They were all grateful for the generous appreciation of their efforts. The Royal Society had been an *Alma Mater* to him from his boyhood. He had profound reverence for its purpose and method, and pride in its incomparable achievements. (Cheers).

Prof. Harold Dixon, who also responded, said the medallists felt that the honour had been paid to them not so much for their own personal achievements, but because they had tried to encourage others to seek out new knowledge. They all rejoiced in that impersonal recognition of their work.

Sir David Gill, in proposing the toast of "The Guests," said they realised that in the American Ambassador they had a man who had helped to promote those international relations in science which were so important for its progress. In coupling the toast with the name of Lord Sumner he said they offered him their warmest congratulations on the recent honour conferred on him. They also congratulated the highest Court of Appeal in the land on a valuable acquisition to its ranks.

Lord Sumner, in responding, said that never before had he seen assembled in one room so many of the immortals of our race, and never before had he met so many seekers after truth. It was a special pleasure to one of his profession, the members of which did not pursue truth in their sense of the word, to come in contact with so distinguished and ancient a body who devoted themselves to the pursuit of truth for its own sake, and knowledge for its own sake.

CHEMICAL SOCIETY.

(Continued from p. 269).

229. "*Methylation of Cellulose.*" By William Smith Denham and Hilda Woodhouse. (*Trans.*, 1913, 1735).

When alkali-cellulose, prepared by mixing cellulose with sufficient 15 per cent solution of sodium hydroxide to give a mixture in which the proportions of the constituents are represented by the ratio $C_6H_{10}O_5 : 2NaOH$, is treated with excess of methyl sulphate a methylated cellulose is obtained, which retains the fibrous structure of the original material and has the composition represented by the empirical formula $C_{12}H_{19}O_9 \cdot OMe$. If this substance is subjected to a repetition of the same treatment the composition of the new product is given by the formula $C_6H_9O_4 \cdot OMe$, whilst another repetition of the process yields a substance the composition which is given by the formula $C_{24}H_{35}O_{15}(OMe)_5$. All these substances can be acetylated, giving derivatives in which the methyl group is still present. The substance $C_6H_9O_4 \cdot OMe$ has been converted into a material which resembles viscose.

230. "*Structure of the Salts of Nitrophenols.*" By John Theodore Hewitt, Rhoda Marianne Johnson, and Frank George Pope. (*Trans.*, 1913, 1626).

An attempt has been made to attack the problem of the constitution of the nitrophenolates on chemical grounds. The sodium derivatives of true phenols react in absolute alcoholic solution with ethyl chloroacetate at water-bath temperatures, giving ethyl aryloxyacetates. Even 2 : 4 : 6-tribromophenol is not sterically hindered, but *o*- and *p*-nitrophenols do not react under the conditions mentioned. Sodium *m*-nitrophenolate, however, gives a good yield of ethyl *m* nitrophenoxyacetate.

The nitro-group in the nitrophenolates is evidently also affected; whilst sodium methoxide reduces nitrobenzene to azoxybenzene and nitroanisole to azoxyanisole, the nitrophenols are not converted into azoxyphenols.

231. "*Neutral and Acid Oxalates of Potassium.*" By Harold Hartley, Julien Drugman, Charles Archibald Vlieland, and Robert Bourdillon. (*Trans.*, 1913, 1747).

A further study has been made of the equilibrium of the system potassium hydroxide-oxalic acid-water, confirming in the main the results of previous investigators, but explaining some discrepancies in their work, for example, the anomalous solubility curve of the neutral oxalate, the degree of hydration of potassium hydrogen oxalate, and the transition temperature of the two modifications of the latter salt. A crystallographic examination has been made of tetrapotassium dihydrogen oxalate, and of a twinned form of the neutral oxalate.

232. "*Adiabatic and Isothermal Compressibilities of some Liquids between One and Two Atmospheres Pressure.*" By Daniel Tyrer. (*Trans.*, 1913, 1675).

A method is described by which the adiabatic compressibility of a liquid can be accurately determined at a pressure of 1 to 2 atmospheres. This consists in principle of compressing the liquid contained in a suitable vessel and observing directly the volume change which occurs, in a calibrated capillary tube. Measurements have been made over a temperature change of 0° to the boiling-poin for the following nine liquids;—Ether, chloroform, carbo

tetrachloride, benzene, toluene, chlorobenzene, carbon disulphide, ethyl alcohol, and water.

By aid of the following thermodynamic equation values have been obtained for the isothermal compressibility : —

$$\beta = \alpha + \frac{T\left(\frac{dv}{dt}\right)^2}{JvC_p},$$

where β is the isothermal compressibility, α the adiabatic compressibility, T the temperature on the absolute scale, v is the specific volume, J the mechanical equivalent of heat, and C_p is the specific heat at constant pressure. The results are compared with the few results already determined by the direct method at low pressures, and a fairly good agreement is found.

233. "*The Constitution of Aconitine.*" By OSCAR LISLE BRADY. (*Trans.*, 1913, 1821).

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 289).

234. "*Methylation of Quercetin.*" By ARTHUR GEORGE PERKIN. (*Trans.*, 1913, 1632).

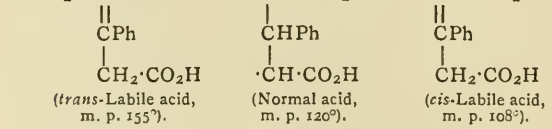
Although owing to the presence of an hydroxyl group adjacent to the carbonyl group it has not hitherto been considered possible fully to methylate quercetin by means of methyl iodide and alkali, no difficulty in reality exists in preparing a quantity of quercetin pentamethyl ether by this method, provided that an excess of the reagents is employed. This substance is to be found dissolved in the aqueous liquid obtained when the product of the reaction is diluted with water, and may be separated therefrom by treatment with salt. Small amounts of substances soluble in ether are simultaneously produced, namely, *methylquercetin tetramethyl ether*, $C_{20}H_{20}O_7$, yellow needles (m. p. 184—185°), which yields an *acetyl* derivative, $C_{20}H_{19}O_7Ac$, colourless needles (m. p. 178—180°), and a yellow *potassium* salt, decomposed by water, and *methylquercetin pentamethyl ether*, $C_{21}H_{22}O_7$, colourless needles (m. p. 213—215°). By hydrolysis the former gives methylphloroglucinolmonomethyl ether (*Trans.*, 1900, lxxvii., 1318) and veratric acid, whereas from the latter a substance considered to be *methoxymethylfisetol dimethyl ether;* colourless needles (m. p. 148—149°) (compare Herzig, *Ber.*, 1909, xlii., 155), and veratric acid are produced.

235. "*Absorption Spectra of Various Derivatives of Aniline, Phenol, and Benzaldehyde.*" By JOHN EDWARD PURVIS. (*Trans.*, 1913, 1638).

A comparative study has been made of the absorption spectra of the vapours and alcoholic solutions of *o*-, *m*-, and *p*-bromoaniline, *o*-, *m*-, and *p*-iodoaniline, 2 : 4-dichloroaniline, *p*-bromophenol, *p*-iodophenol, 2 : 4 : 6-trichlorophenol, 2 : 4 : 6-tribromophenol, *m*-aminophenol, *m*-dimethylaminophenol, *p*-aminobenzaldehyde, and *p*-dimethylaminobenzaldehyde.

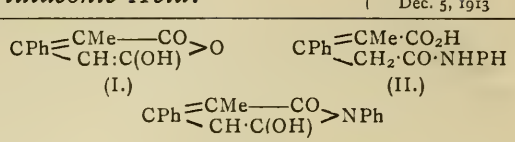
236. "*Chemistry of the Glutaconic Acids.* Part VIII. *β-Phenylglutaconic Acid and the β-Phenyl-α-methylglutaconic Acids.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD. (*Trans.*, 1913, 1569).

β-Phenyl-α-methylglutaconic acid has been isolated in three distinct modifications, which can be represented by the following formulæ :—



(*trans*-Labile acid, m. p. 155°). (Normal acid, m. p. 120°). (*cis*-Labile acid, m. p. 108°).

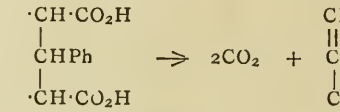
The *trans*-labile acid is stable towards acetyl chloride, but both the normal acid and the *cis*-labile acid are converted by this reagent into the hydroxy-anhydride (I.) (m. p. 94°), which yields the anilic acid (II.) (m. p. 143°), and the hydroxy-anil (III.) (m. p. 216°) with aniline.



(I.) (II.) (III.)

The *trans*-labile acid is converted into the sodium salt of the *cis*-labile acid by alkali hydroxide, and both the *cis*-labile acid and the *trans*-labile acid are converted into the normal acid by hydrochloric acid. The hydroxy-anhydride is converted into the normal acid by boiling water and into the *cis*-labile acid by alkali in the presence of casein. The three modifications of the acid are readily distinguished by the aid of their barium salts.

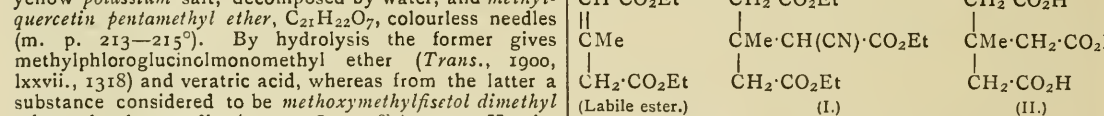
The acids of this type readily undergo decomposition when boiled with dilute mineral acids, and yield the corresponding hydrocarbon, thus : —



(β-Phenylglutaconic acid). (*iso*Propenylbenzene).

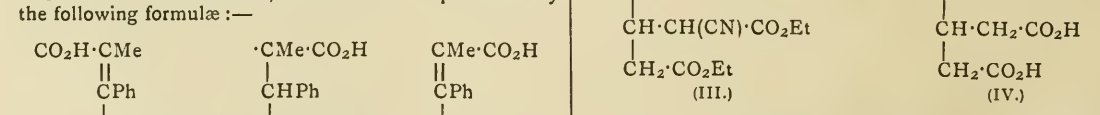
237. "*The Chemistry of the Glutaconic Acids.* Part IX. *A Method for Distinguishing between the Esters of the Normal and Labile Acide.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD. (*Trans.*, 1913, 1579).

The ester of a labile acid can be readily distinguished from its normal isomeride by the capacity it possesses of forming a condensation product with ethyl sodiocyanoacetate; thus the labile ethyl ester of β-methylglutaconic acid forms the condensation product (I.) to the extent of 60 per cent, whereas the corresponding normal ester under similar conditions yields no trace of this substance :—

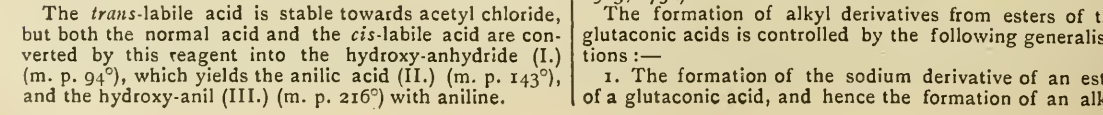


(Labile ester.) (I.) (II.)

The condensation product yields *ββ-dimethylpropanetricarboxylic acid* (II.) on hydrolysis, and derivatives of this compound have been prepared. Several normal esters of the series were investigated, but were found to yield no trace of a condensation product. Normal ethyl glutaconate, which is capable of passing, with considerable ease, into derivatives of the unstable labile ester, yields with ethyl sodiocyanoacetate about 5 per cent of the condensation product (III.) from which iso*butane-αγγ'-tricarboxylic acid* (IV.) can be isolated on hydrolysis :—



(Normal ester.) (Labile ester).



(III.) (IV.)

238. "*The Chemistry of the Glutaconic Acid.* Part X. *The Alkylations of the Ethereal Salts.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD. (*Trans.*, 1913, 1752).

The formation of alkyl derivatives from esters of the glutaconic acids is controlled by the following generalisations :—

1. The formation of the sodium derivative of an ester of a glutaconic acid, and hence the formation of an alkyl

derivative, takes place through the labile form of the ester alone.

2. The normal esters, as such, do not react with sodium ethoxide.

3. The formation of a sodium derivative of a normal ester is therefore dependent on the tendency for the ester to pass into the labile modification under the experimental conditions employed.

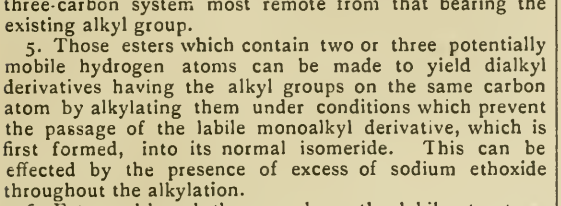
4. The formation of a sodium derivative from a normal ester of a monoalkylated dicarboxylic acid involves the passage of the mobile hydrogen atom to the carbonyl system not affected by the substituting group. The second alkyl group therefore enters on the carbon atom of the three-carbon system most remote from that bearing the existing alkyl group.

5. Those esters which contain two or three potentially mobile hydrogen atoms can be made to yield dialkyl derivatives having the alkyl groups on the same carbon atom by alkylating them under conditions which prevent the passage of the labile monoalkyl derivative, which is first formed, into its normal isomeride. This can be effected by the presence of excess of sodium ethoxide throughout the alkylation.

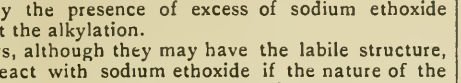
6. Esters, although they may have the labile structure, will not react with sodium ethoxide if the nature of the groups carried by the carbon atoms of the three-carbon system is such as to prevent the movement of the hydrogen atom within the molecule.

239. "*The Formation and Reactions of Imino-compounds.* Part XVIII. *The Condensation of* cyclo*Hexanones with Cyanoacetamide Involving the Displacement of an Alkyl Group.*" By Jocelyn Field Thorpe and Arthur Samuel Wood. (*Trans.*, 1913, 1586).

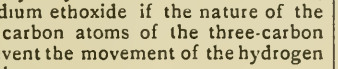
Whereas 3-methyl*cyclo*hexanone and 4-methyl*cyclo*hexanone yield condensation products with cyanoacetamide from which 3-*methyl*cyclo*hexane*-1 : 1-*diacetic acid* (I.) and 4-*methyl*cyclo*hexane*-1 : 1-*diacetic acid* (II.) can be prepared in large quantity, 2-methyl*cyclo*hexanone and 1 : 3-dimethyl*cyclo*hexane-4-one condense with the amide to form *cyclo*hexane-1 : 1 diacetic acid (III.) and 4-methyl-*cyclo*hexane-1 : 1-diacetic acid (II.) respectively.



(I.)



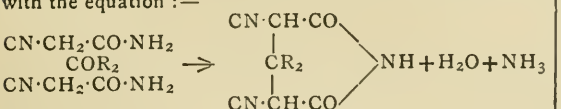
(II.)



(III.)

Since great care was taken to use these ketones in a very pure form, it follows that the presence of the methyl group in the 2-position inhibits condensation, but that the tendency for the formation of a condensation product is so considerable that it is effected through the displacement of this group, probably as methyl alcohol.

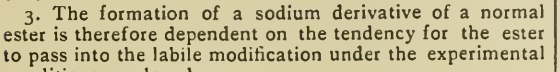
The by-products formed to the extent of about 10 per cent in the reactions between the ketones and cyanoacetamide are the cyano imides (IV.) formed in accordance with the equation :—



(IV.)

240. "*The Replacement of Alkyl Groups in Tertiary Aromatic Bases.*" By Jocelyn Field Thorpe and Arthur Samuel Wood. (*Trans.*, 1913, 1601).

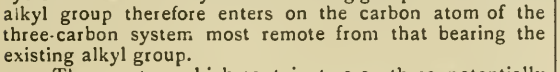
Experiments are described showing the unsuitability of the bases diethyl- and dimethyl aniline for the purpose of eliminating hydrogen haloid from substances capable of parting with these elements. It is shown, for example, that there is always a tendency for the base to combine with the halogen derivative, forming a quaternary salt, and that when once this salt is formed a decomposition represented by the equation—



(Quaternary salt).

ensues on heating.

In the case of those substances which are not capable of eliminating hydrogen haloid, the formation of the quaternary salt and its decomposition in accordance with the equation—



is quickly completed.

The reactions between the dialkylanilines and both trimethylene bromide and ethylene dibromide are also described.

241. "*Coumaranone Derivatives.* Part II. *The Constitution of Ethyl Coumaranonecarboxylate.*" By Richard William Merriman. (*Trans.*, 1913, 1838).

Several distinct observations indicate that ethyl coumaranonecarboxylate normally exists in the enolic form $C_6H_4<\overset{\text{—O—}}{\underset{C(OH)}{}}\!\!>C\cdot CO_2Et$. (*a*) During many subsequent attempts to prepare the phenylhydrazone described in Part I. (*Trans.*, 1911, xcix., 911) an isomeric substance, $C_6H_4<\overset{\text{———O———}}{\underset{C(NH\cdot NHPh)}{}}\!\!>C\cdot CO_2Et$, was always obtained. (*b*) An oxime could not be isolated. (*c*) Exactly one equivalent of sodium hydroxide was required to neutralise the ester. (*d*) It reacts towards Grignard's reagent entirely in the enolic form. (*e*) The absorption curves of the ester and its acetyl derivative are practically identical. The addition of alkali completely alters the character of the absorption spectrum. This fact has been explained by the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (*Trans.*, 1913, ciii., 415).

o-*Carbamylphenoxyacetic acid*,—

$$NH_2\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

was prepared during this investigation.

242. "*Coumaranone Derivatives.* Part III. *Acylazo-derivatives of Coumaranonecarboxylic Acid.*" By Richard William Merriman. (*Trans.*, 1913, 1845).

Benzeneazocarbonylcoumaranone,—

$$C_6H_4<\overset{\text{—O—}}{\underset{C(OH)}{}}\!\!>C\cdot CO\cdot N{:}NPh,$$

and its phenyl hydrazone,—

$$C_6H_4<\overset{\text{———O———}}{\underset{C(:N\cdot NHPH)}{}}\!\!>CH\cdot CO\cdot N{:}NPh$$

(Part I., *Trans.*, 1911, xcix., 911), have been subjected to further investigation, the results of which confirm the formulæ assigned to them.

An acetate and metallic derivatives of benzeneazocarbonylcoumaranone have been prepared. By reducing an alkaline solution of the orange azo-compound with zinc dust the colourless hydrazo-derivative,—

$$C_6H_4<\overset{\text{·O·}}{\underset{CO}{}}\!\!>CH\cdot CO\cdot NH\cdot NHPh,$$

was obtained. When stannous chloride or sodium hyposulphite was used as the reducing agent, the azo-group was broken, with the liberation of aniline.

The red azophenylhydrazone also forms an acetate and metallic derivatives. This phenylhydrazone is extremely resistant towards all hydrolytic agents, except fuming hydrobromic acid, which converts it into the parent azo-compound.

Similar colourless hydrazo-compounds, orange azo-

compounds, and red hydrazones of the latter have been prepared by using the three tolylhydrazines in place of phenylhydrazine.

The absorption spectra of the above compounds have been measured and compared with those of *s*-benzoylphenylhydrazine, NHBz·NHPh, and Fischer's benzoylazobenzene, NBz:NPh.

243. "*The Dynamics of Bleaching.*" By SYDNEY HERBERT HIGGINS. (*Trans.*, 1913, 1816).

Experiments on the bleaching of linen cloth containing a large excess of colouring matter, by means of very dilute bleaching powder solution, show that the bleaching action proceeds in accordance with the equation $HOCl = HCl + O$, and is thus a unimolecular reaction.

The influence of adding lime-water or hydrochloric acid to the bleaching solution was also studied.

(To be continued).

INSTITUTE OF CHEMISTRY.

AT a meeting of the Institute of Chemistry held at the Imperial College of Science and Technology, South Kensington, on Wednesday, November 26, the second lecture on "*The Research Chemist in the Works, with Special Reference to the Textile Industry*" was delivered by Mr. W. P. DREAPER, F.I.C. Dr. George McGowan, Vice-President, in the Chair.

Continuing his subject, the lecturer called attention to the importance of a knowledge of theory, and illustrated this point specially by a reference to the work done in connection with the presence of stains and loss of strength experienced on the storage of certain silk goods. This was found to be due to the free sulphuric acid. Only a knowledge of theory had suggested why this could be present in cases where this acid had never been used in any process of manufacture. The so-called "neutral salt reaction" had offered a solution to this problem, and has relieved the dyer from constant blame.

The British aniline dye industry had recently made remarkable progress, and its products were even being sold in Germany. The future would see considerable expansion in this reviving industry.

The work of the textile chemist was further illustrated by reference to the manufacture of crêpe de chine, and the part played by the chemist in the production of the "crape" effect, and its retention through subsequent processes of manufacture.

Dealing generally with the subject of embossing, attention was drawn to the evolution of what was known as mourning crape, with its extremely complicated process of manufacture. Some fifty years ago a Tottenham weaver attempted to improve upon the product as then imported from China, which was of the nature of a rough silk material. This weaver attempted to make it more realistic by representing on its surface "the tears of the mourners." This was accomplished by passing the cloth and a long length of fishing net through a pair of rollers. This original design can be detected upon the modern products, although in almost every other respect the manufacture has changed. Under modern conditions the chemist is required to direct every step from the raw material to the final waterproofing process.

The processes of bleaching cotton, as used to-day, were then described aud illustrated by samples, and the principles involved in dyeing, finishing, and printing fabrics were touched on.

When the chemist produced results in the laboratory and desired to see them reproduced on a large scale, it was essential that he should be in a position to indicate to the engineer the nature of the machinery required; better still, to submit a design for the same. The method of attack adopted by the chemist was so essentially different, in its direction and nature, from that adopted by the engineer that this alone justified his presence in any works. It also defined the relative position of the chemist and engineer; it was sometimes necessary for the chemist to retain control of certain industrial processes which had emanated from the laboratory, especially when these were more dependent upon chemical factors than mechanical or electrical ones; thus the chemist became directly involved in working conditions and industrial operations.

The influence of the chemist on the choice of raw materials should be greatly extended. This point had received attention in certain quarters. The South African Government still recommended the use of a sheep-dip which seriously reduced the value of South African wool and gave great trouble in subseqnent manufacture. This matter had been repeatedly brought to their notice.

In conclusion, it was pointed out that a rigidly chemical training was an insufficient equipment for the modern investigator. He would either find himself working over long periods in other directions, or failing to follow up investigations just when they became interesting and profitable. Given a suitable subject almost everything depended upon attention to detail.

For the right man properly trained the textile industry offered a good opening, when the worker concerned himself with problems of general interest rather than with factory detail, the matching of colours, and the like. Many chemists wasted their early years of research on matters which, although important in themselves, led nowhere. This should be avoided whenever possible.

The lecture was illustratad by examples of machinery used, samples of textile materials in the intermediate stages of manufacture, and actual demonstrations of hand, block, and spray printing.

CORRESPONDENCE.

GALLIUM: ITS WIDE DISTRIBUTION, &c.

To the Editor of the Chemical News.

SIR,—Two French chemists have recently observed the presence of gallium in commercial aluminium, and it has been announced as a new discovery (Boulanger and Bardet, Academy of Sciences, October, 27, 1913; CHEM. NEWS, cviii., 232). I feel it is necessary to call attention to the fact that the presence of gallium in aluminium was first observed by the late Prof. Sir Walter N. Hartley and myself as far back as 1897 (*Trans. Chem. Soc.*, 1897, p. 547).

It may interest Mr. F. H. Loring (CHEM. NEWS, cviii. 247) to know that during the years 1895—9, the presence of gallium was also discovered in iron, in many iron ores, in siderite, aluminous minerals, manganese ores, very many silicates and other minerals, in dust from various sources, &c., and in meteorites, and its presence in the sun was also established. It is, in fact, one of the most widely distributed elements, but in no case has it been discovered in large quantity.

I have recently, after an interval of nearly ten years in which research has been practically impossible, begun a search for the richest source of gallium.—I am, &c.,

HUGH RAMAGE.

Technical Institute, Norwich.

THE NEW AMERICAN DUTY TARIFF.

To the Editor of the Chemical News.

SIR,—As we are still receiving enquiries from manufacturers and others, it is evident that many business houses are still unfamiliar with the duties now payable on the goods in which they are concerned.

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NOTICES OF BOOKS.

Outlines of Mineralogy. By GREVILLE A. J. COLE. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THIS book is intended chiefly for students of geology, and will serve them excellently as an introductory course in mineralogy. The characters of minerals are described in Part I., which contains a short outline of the principles of crystallography and also a clear account of methods of investigating the optical characters of minerals. In the second part of the book the minerals are first classified as ores of the elements arranged according to the periodic system, and then comparatively full data are given of the individual minerals.

A Treatise on Quantitative Inorganic Analysis with Special Reference to the Analysis of Clays, Silicates, and Related Minerals. Vol. I. By J. W. MELLOR, D.Sc. London: Charles Griffin and Co., Ltd. 1913.

THOSE chemists who are specially interested in the analysis of the materials employed in the ceramic industries should not fail to get a copy of this work, which will at once take its place in scientific literature as the standard work on the subject. The author's experience in the Testing Department of the County Pottery Laboratory, Staffordshire, has given him unique opportunities of testing different methods and working out schemes for the analysis of silicates, &c., and many of the processes described have been employed for years, after having been modified in accordance with the experience of students in the analytical classes and of the professional staff. The author has also kept pace with the ever-growing mass of literature on the subject, and in extensive footnotes gives an enormous number of references to English and foreign periodicals. He writes in a graphic style, and is a great believer in the value of paying attention to the smallest details. The causes of faulty results in analytical work and want of agreeement between the results of different workers are very helpfully discussed.

Quantitative Analysis in Practice. By JOHN WADDELL, B.A. (Dalhousie University), B.Sc. (London), Ph.D. (Heidelberg), D.Sc. (Edinburgh). London: J. and A. Churchill. 1913.

THE methods described in this text-book of quantitative analysis have been selected as being suitable for the elementary work both of technical students and of those who are intending to devote themselves to the pure science. They include some gravimetric methods for common metals and acid radicles, such as Ba, Mg, Cl, SO_4, and also the analysis of complex substances, such as limestones, clays, &c. The electrolytic determination of copper is described, as well as some volumetric methods and their applications to certain ores. The author lays great stress upon the need for forethought and economy of time, and the actual times necessary for each analysis and in some cases for the separate steps of it are stated. Thus, although accuracy is given first place as the aim which should be pre-eminent in the student's mind, he is kept up to the mark as regards speed, and the book will provide a specially good training for technical analysts.

The Chemical Trade. Pitman's Specialised Correspondence Books. London, Bath, and New York: Sir Isaac Pitman and Sons, Ltd.

THIS little book will provide the shorthand writer or typist who is in a chemist's office with a certain amount of material by means of which he can make himself acquainted with the terms, &c., employed in the business. It contains more than forty letters and market reports dealing with the chemical industries, marked off in twenties for the purposes of dictation, and if the shorthand typist studies them carefully and follows the editor's advice regarding the setting out of statistical matter on a typewriter, the working out of calculations involving the English and metric systems and similar details, he will increase his efficiency and add to his chance of promotion to a more responsible position. It is pointed out that a knowledge of the science is most valuable, to enable him to correct errors on the part of his employer, and he is given, perhaps unintentionally, at least one chance of performing the same office for his text-book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Academie des Sciences. Vol. clvii., No. 16, October 20, 1913.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 12, 1913.

Titrimetric Determination of Fluorine.—Alfred Greeff.—A solution of ferric chloride produces a white crystalline precipitate of general formula $[FeF_6]X_3$ in neutral aqueous solutions of alkali fluorides. Sodium iron fluoride is only very slightly soluble in water, and does not give the characteristic red colouration with sulphocyanides. To determine fluorine 0·5 grm. of the substance are dissolved in 25 cc. of hot water, about 25 grms. of sodium chloride are added to the cooled solution, and about 5 cc. of sulphocyanide solution. The solution is then titrated with iron chloride solution till it becomes pale yellow. Ten cc. of alcohol and 10 cc. of ether are added, and more iron chloride solution is carefully run in until after shaking and allowing to stand the red colouration still persists. Every molecule of $FeCl_3$ used corresponds to six molecules of NaF. The solution of fluoride used must be neutral to phenolphthalein. Solutions of sodium silicofluoride or of acid sodium fluoride must first be treated with caustic soda, when the neutral fluoride will be obtained:—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O,$$
$$NaF.HF + NaOH = 2NaF + H_2O.$$

Action of Sulphur Trioxide on Salts.—Wilhelm Traube.—When sodium chloride is subjected to the action of sulphur trioxide the product is the sodium salt of chlorpyrosulphonic acid, $NaCl + 2SO_3 = \begin{matrix} O_2.S.ONa \\ O_2.S.Cl \end{matrix} > O$. Sodium chlorsulphonate, $NaClSO_3$, is undoubtedly formed as an intermediate product. Sodium fluoride gives with sulphur trioxide addition products, which are quite different from those obtained from the chlorides. Their aqueous solutions are neutral, and they do not give the reactions of either hydrofluoric or sulphuric acids. These salts are derived from fluosulphonic acid. Nitrites absorb SO_3, giving salts of nitrosotrisulphonic acid, *e.g.*, $NO_2(SO_3)_3Na$, and persulphates behave similarly, the products being probably perpyrosulphates, $K_2S_2O_8 + 2SO_3 = KS_2O_6.O_2.S_2O_6K$.

Aromatic Compounds containing Selenium.—R. Lesser and R. Weiss.—When thionyl chloride or phosphorus pentachloride acts on diphenyl diselenide, di-*o*-carboxyllic acid, besides the chloride, an addition produc of formula $\left(\begin{matrix} H \\ Cl \end{matrix}\!>\!Se.C_6H_4.CO.Cl\right)_2$, is obtained. This indicates that the group Se.Se possesses very strongly basic properties and is capable of forming salts. The authors have prepared a series of indigoid dyes derived from 3-oxyselenonaphthene, and also a number of condensation products of the latter, chiefly with aldehydes.

Cerium Dioxide as Contact Substance in Organic Combustions.—Julius Bekk.—Cerium dioxide acts as a catalyst in the combustion of gases, and it can conveniently be used in quantitative experiments by Dennstedt's method. Asbestos impregnated with the oxide is prepared by soaking pure asbestos in a concentrated solution of cerous nitrate and then igniting.

Separation of Halogen Hydride by Phosphorus Pentoxide.—H. Lecher. — Phosphorus pentoxide acts energetically as a catalyst in the separation of halogen hydrides. Thus, if benzoyl chloride is warmed with excess of naphthalene no reaction occurs, but if a small quantity of phosphorus pentoxide is added, HCl is at once evolved, and a 90 per cent yield of α- and β-naphthyl phenyl ketone is obtained. Only small quantities of the catalyst are needed and large amounts have an unfavourable effect. One drawback of the new catalyst is the high temperature at which the reactions occur.

Atomic Weight of Yttrium.—R. J. Meyer and M. Weinheber.—The authors have carried out a new series of atomic weight determinations as follows:—They dissolved the oxide in a little nitric acid in a platinum dish, added rather more than the calculated amount of sulphuric acid, and evaporated to crystallisation. The octohydrate, $Y_2(SO_4)_3+8H_2O$, then separated in clear monoclinic crystals. The mother-liquor was then poured off and the crystals washed with ice-water and then dehydrated by heating to 300–400°. The anhydride thus obtained was dissolved in water and the solution evaporated. This operation was repeated twice. The crystalline salt thus obtained is quite neutral. Some of it was weighed in a platinum crucible and heated to 400° in an electric furnace, and thus dehydrated to constant weight. The sulphate was then converted into oxide by heating before the blowpipe. The results thus obtained agree very well, and the most probable value of the atomic weight is 88·7.

Oxidation of Coals at Moderate Temperatures.—K. A. Hofmann, K. Schumpelt, and K. Ritter.—The anthors have already reported that amorphous coal is oxidised by chlorate solutions, made active by means of osmium tetroxide, at the temperature of the water-bath, the products being carbon dioxide, mellogen, and mellitic acid. In further experiments they have now found that carbon is much more readily oxidised at moderate temperatures than has been supposed. Thus a dilute aqueous solution of calcium hypochlorite acts energetically on it, the products being carbon monoxide and dioxide. Amorphous carbon in presence of alkalis at 120—150° gives dark brown and red colloids, and then yields formate and oxalate, and finally carbonate.

Preparation of Pure Anhydrous Selenium Dioxide, and the Atomic Weight of Selenium.—Josef Jannek and Julius Meyer.—Selenium dioxide can readily be oxidised by a mixture of N_2O_4 and oxygen, and no trace of the hypothetical SeO_3 nor of the acid is formed. The N_2O_4 acts simply as a carrier of oxygen, as in the lead chamber process. Between 400° and 500° SeO_2 can be sublimed unchanged, but at higher temperatures it is decomposed. This method of oxidising selenium provides a convenient process for determining the atomic weight of selenium. The results obtained are Se=79·158 in air and Se=79·141 *in vacuo*.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 1st inst.; the Duke of Northumberland, President, in the Chair. Mr. Howard Marryat and Mr. H. Gordon Selfridge were elected Members, and Dr. Henri Deslandres (Paris) was elected an Honorary Member of the Institution. The Chairman announced the decease of Sir William Preece, a Member of the Institution, and a resolution of condolence with the family was passed.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, before Easter:—Prof. H. H. Turner, Savilian Professor of Astronomy, Oxford, a course of experimentally illustrated lectures, adapted to a juvenile auditory, on "A Voyage in Space: The Starting Point—Our Earth," December 27; "The Start through the Air," December 30; "Journeying by Telescope," January 1; "Visits to the Moon and Planets," January 3; "Our Sun," January 6; "The Stars," January 8. Prof. W. Bateson, Fullerian Professor of Physiology, Royal Institution, six lectures on "Animals and Plants under Domestication," Prof. Sir John H. Biles, three lectures on "Modern Shipbuilding—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy." Mr. Arthur H. Smith, two lectures on "Landscape and Natural Objects in Classical Art." Dr. W. McDougall, two lectures on "The Mind of Savage Man (Illustrated by the Pagan Tribes of Borneo—(1) His Intellectual Life; (2) His Moral and Religious Life." Prof. Sir Thomas H. Holland, two lectures on "Petroleum Supply from the Geological Point of View." Prof. I. Gollancz, two lectures on "Hamlet in Legend and Drama—(1) The Myth; (2) The Play." Prof. C. F. Jenkin, three lectures on "Heat and Cold." Dr. C. W. Saleeby, two lectures on "The Progress of Eugenics—(1) The First Decade of Modern Eugenics, 1904—14; (2) Eugenics To-day— Its Counterfeits, Powers, and Problems." Prof. F. Corder, three lectures on "Neglected Musical Composers—(1) Ludwig Spohr; (2) Henry Bishop; (3) Joachim Raff" (with Musical Illustrations). Dr. J. A. Harker, two lectures on "The Electric Emissivity of Matter—(1) The Metals; (2) Other Substances" (with Experimental Illustrations). Prof. Sir J. J. Thomson, Professor of Natural Philosophy, Royal Institution, six lectures on "Recent Discoveries in Physical Science." The Friday Evening Meetings will commence on January 23, when Prof. Sir James Dewar will deliver a Discourse on "The Coming of Age of the 'Vacuum Flask.'" Succeeding Discourses will probably be given by Mr. H. Wickham Steed, Dr. H. S. Hele Shaw, Prof. J. Norman Collie, Prof. W. A. Bone, Rev. Canon J. O. Hannay ("George A. Birmingham"), Sir Walter R. Lawrence, Bart., the Right Hon. Lord Rayleigh, Prof. J. A. Fleming, Prof. Sir J. J. Thomson, Dr. A. Keith, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof. E. G. Coker, D.Sc.

TUESDAY, 9th.—Biochemical Society, 5.30. (At the Lister Institute, Chelsea Gardens, S.W.).

WEDNESDAY, 10th.—Royal Society of Arts, 8. "Applications of Electricity to Agriculture and Life," by T. Thorne Baker.

THURSDAY, 11th.—Royal Society. "Intermittent Vision," by A. Mallock. "Relations between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution," by W. Wahl. "Selective Absorption of Ketones," by G. G. Henderson and J. M. Heilbron.. "Absolute Measurements of a Resistance by a Method based on that of Lorenz," by F. E. Smith. "Determination of the Electromotive Force of the Weston Normal Cell in Semi-absolute Volts," by A. N. Shaw. "Elastic Hysteresis in Steel," by F. E. Rowett. "Simple Form of Micro-balance for Determining the Densities of Small Quantities of Gases," by F. W. Aston. "A Second Spectrum of Neon," by T. R. Merton.

FRIDAY, 12th.—Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Alchemy in China," by Prof. H. Chatley, B.Sc.

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THE CHEMICAL NEWS.

Vol. CVIII., No. 2820.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

(Concluded from p. 273).

A systematic investigation by F. Foerster and J. Yamasaki (*Zeit. Elektrochem.*, 1910, xvi., 321) of the phenomena which accompany the discharge of bromine from neutral and alkaline potassium bromide solutions, had established that the anodic discharge of bromine ions from platinised platinum anodes was only then reversible, when the anode in question was free from any oxygen charge. When, however, the anode was charged with oxygen, be that by anodic polarisation or by a liberation of oxygen during the electrolysis of the bromide, the discharge of the bromine took place at potentials considerably more noble than those one might have expected for the reversible reaction from the observed bromine potentials. Thus an oxygen content of the platinised electrode retards the discharge of the bromine ions.

Quite recently F. Foerster and F. Herrschel (F. Herrschel, "Dissertation," Leipzig, 1912) have also studied

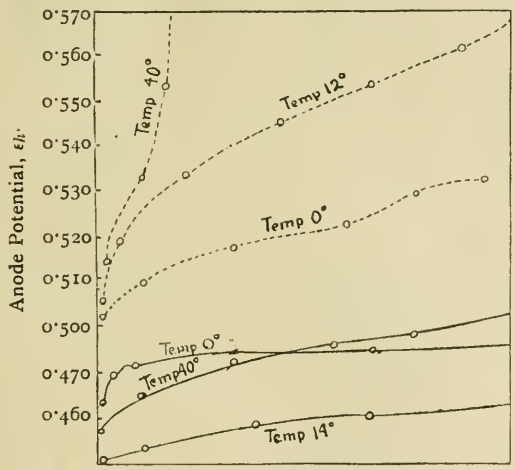


Fig. 5.

the retardation of the iodine discharge from iodide solutions. The electrolysis of neutral and of alkaline solutions of potassium iodide, it resulted, did not in general prove strictly reversible. The anode showed temporarily increasing polarisations, much more intense than concentration effects, and this temporary rise of the potential was much greater with smooth platinum anodes than with platinised anodes. The increase further grew with rising temperature and increasing current density. The polarisation was further more marked when the concentration ratio C_{OH}'/Cz' of the alkaline solution was increased.

The temperature influence upon the anode potential, as well as the difference in the potentials with smooth and with platinised platinum, can be seen from Fig. 5. The anode potentials are plotted against the electricity quantities expended, measured with a current intensity of 1 ampère and with smooth and platinised platinum at different temperatures in a solution which was normal as to KI and 0·9 normal as to iodine. The full curves refer to platinised platinum, the dotted curves to smooth platinum. We see that the polarisation is much stronger with the smooth platinum, and further that a rise of temperature calls forth a material increase in the polarisation. That the marked temporary rise in the polarisation, also with the iodine discharge, was indeed due to an oxygen charge on the anode, was proved by the comparison between the polarisation of a cathodically pre polarised platinised electrode free from oxygen and the polarisation of an anodically polarised electrode charged with oxygen. The result of one of these experiments, performed with a solution normal as to KI, 0·9 normal as to iodine, at ordinary temperature, is reproduced in Fig. 6. We see at once how great the increase in the polarisation is which has been produced by charging the anode with oxygen.

The experiments alluded to leave no more doubt that the retardations, which occur when bromine and iodine are discharged from neutral or alkaline solutions of bromide or iodide, are to be traced back to an oxygen charge on the anode. When looking for an explanation of this interesting phenomenon we shall first have to consider the process of the oxygen evolution carefully. This evolution, it has long been known, does not represent a reversible process. Whilst we should expect the evolution to take

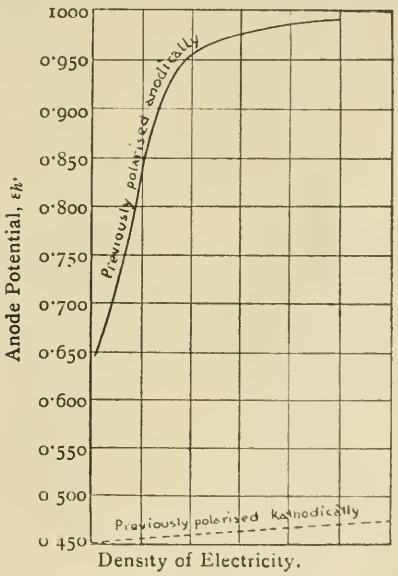


Fig. 6.

place in 2N-H_2SO at a potential $eh = +1{\cdot}23$ volt, it is so much retarded that, at a platinised anode, it does not set in before $eh = +1{\cdot}5$ volt, and the potentials have further to be raised when the evolution is continued. Thus the oxygen evolution shows, like the discharge of the halogens, a temporary strong rise of the polarisation value. To understand this retardation of the anodic oxygen liberation we must assume, following F. Foerster's theory (*Zeit. Phys. Chem.*, 1909. lxix., 236), that the potential of the electrode depends upon the anodically discharged oxygen which forms an unstable primary oxide, PtO_x, with the platinum. This oxide is soluble in the finely distributed platinum of the platinised electrode, and passes, under evolution of oxygen, into a more stable lower oxide, PtO perhaps. The latter is again soluble in the finely distributed platinum. We have now to assume that the rate of decomposition of the primary oxide is diminished in the same measure as

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12, 1913.

he concentration of the stable oxide on the surface of the electrode increases. In order then to maintain a constant current density, *i.e.*, in order always to evolve the same amount of oxygen, the concentration of the primary oxide, and therefore the anode potential, should increase together with increasing formation of the stable oxide on the surface of the electrode. I have been able to demonstrate (G. Grube, *Zeit. Elektrochem.*, 1910, xvi., 621), by comparative potential measurements of the platinum oxides and of platinised platinum electrodes (after polarisation in sulphuric acid), that the anodic evolution of oxygen from platinised electrodes, so far as it takes place below the anode potential $_{eh} = +1{\cdot}6$ volt, is connected with the formation and decomposition of the platinum trioxide, so that PtO_3 would agree with PtO_x. For still higher potentials, observed at platinised electrodes, we must, in order to account for the oxygen evolution, presume the intermediation of a still higher oxide, possibly PtO_4.

After our having thus experimentally demonstrated that the retardation of the anodic oxygen evolution can satisfactorily be explained by the existence of unstable platinum oxides, it would appear plausible that the retarded halogen discharge from platinum electrodes could be accounted for by the aid of intermediate compounds similar to the primary oxides of platinum. Luther and Brislee (*loc. cit.*) already supposed that the discharge of chlorine from smooth platinum might be secondary, via some unknown intermediate product lying between Cl' and Cl_2. If we accept the existence of such a product, by ascribing to platinum a certain solubility for discharged halogen ions, we might imagine that the decomposition of unstable products (which are characteristic for the status nascendi of the halogens) might be impeded by an oxygen charge on the anode in a similar way as we assumed for the decomposition of the primary oxides of platinum (characteristic for the status nascendi of oxygen).

When we review the researches which we have been discussing with regard to their bearing on the theory of passivity, the following main points should be accentuated :—

1. It has been proved that the cathodic deposition of the iron metals—in itself a slowly-progressing reaction—can still more be retarded to a considerable extent by the simultaneous deposition of zinc or of hydrogen. The cause of these retardations is probably to be found in a change of the surface of the electrode, the change being characterised by the formation of unstable intermediate products of higher electrolytic solution pressure than the pure metals possess.

2. The circumstance that cathodic processes can materially be retarded by the occurrence of small quantities of foreign substances on the electrode lends essential support to the assumption that anodic processes may likewise be retarded by the formation of oxygen alloys on the anodes. In many cases therefore the cause of the anodic passivity will not be a mechanical closure (covering up) of the electrode surface by an oxide film, but the formation of an alloy consisting of the material of the anode surface and of oxygen, this alloy having a lower electrolytic solution pressure than the pure metal.

3. In the electrolytic oxidation of ferropotassium cyanide to ferripotassium cyanide a strong polarisation was always observed when the electrodes were surrounded by films of ferrocyanide or of oxides. These strong polarisations were not found with platinum, gold, nickel, cobalt, and copper in alkaline solutions. It may therefore be concluded that, in this latter case, the passivity is caused, not by an oxide film, but by an oxygen alloy on the anode.

4. It has been shown that the retardations observed in the anodic discharge of the halogens are likewise to be ascribed to alloys of the platinum anodes with oxygen.

5. It has been exemplified by the anodic evolution of oxygen what we have to understand by the passivating oxygen alloys. We may imagine that the oxygen combines to a small extent with the anode material to form oxides, which in their turn form, together with the unchanged electrode material, solid solutions, and therefore one-phase systems of continuously variable composition and likewise variable electrolytic solution pressure. The oxide-film theory contrasts with this view, since according to that theory the oxide formed would mechanically cover and shut off the electrode surface so that oxide-film and electrode would form a two-phase system. The oxygen-alloy theory of the passivity thus seeks the cause of the passivity in a change of the chemical properties of the anode material, whilst the oxide-film theory finds the cause in a change of the mechanical properties of the electrode surface.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Continued from p. 274).

III. *Acids, Bases, and Salts of the Ammonia System.*

4. *Compounds Related to Ammonia as the Ordinary Oxygen Acids, Bases, and Salts are Related to Water.*—A consideration of the many points of resemblance between water and liquid ammonia as electrolytic solvents has led the writer to the conception of a system of acids, bases, and salts in which ammonia occupies a position similar to that held by water in its relation to the ordinary oxygen acids, bases, and salts. The compounds bearing such a relationship to ammonia are the acid amides and imides, the metallic amides and imides, and the metallic derivatives of the acid amides and imides respectively. Just as acetic acid, for example, may be looked upon as a derivative of water in which one-half of the hydrogen is replaced by the electronegative radical, acetyl, so acetamide is ammonia in which one-third of the hydrogen is replaced by acetyl; as potassium hydroxide is a derivative of water, so is potassium amide a similar derivative of ammonia; and in the same sense that potassium acetate is derived from water, so potassium acetamide may be regarded as ammonia in which a part of the hydrogen is replaced by potassium and another part by the acetyl group. Finally, the familiar relations existing between the metallic hydroxides and oxides and between acids and acid anhydrides are exemplified, at least formally, in the analogous relationship which the metallic amides and imides, on the one hand, bear to the metallic nitrides, and which the acid amides and imides, on the other hand, bear to the non-metallic nitrides.

5. *Nomenclature.*—The ordinary acids, bases, and salts, which were first recognised by Lavoisier as being oxygen compounds, came later to be looked upon as derivatives of water, and as such constituting what may be called a water system of acids, bases, and salts. Under the influence of the dictum of Lavoisier that oxygen is a never-failing constituent of all acids, chemists assumed that hydrochloric acid, the one known halogen acid, was a hydrated oxide of an unknown element; and it was only after the demonstration of the elementary nature of iodine and chlorine that a class of oxygen-free acids and salts—the halogen acids and salts—came to be clearly recognised. Latterly a limited number of other oxygen-free compounds have come to be recognised as possessing the properties of acids, bases, and salts, conspicuous among them being the sulpho acids, bases, and salts. Certain acid amides have long been known to possess acid properties to the extent, at least, of forming salt-like metallic derivatives, but it is only since the investigations of the writer and his collaborators have demonstrated the acid, basic, and salt-like character of the acid amides, the metallic amides, and the metallic derivatives of the acid amides respectively, that the existence of an ammonia system of acids, bases, and salts must be recognised.

* From *American Chemical Journal*, xlvii., No. 4.

THE WATER OR OXYGEN SYSTEM.

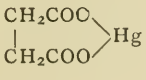
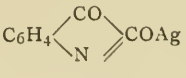
Aquo Acids and Acid Anhydrides.

Acetic acid	CH_3COOH
Acetic anhydride	$(CH_3CO)_2O$
Benzoic acid	C_6H_5COOH
Benzenesulphonic acid	$C_6H_5SO_2OH$
Nitrobenzenesulphonic acid	$C_6H_4(NO_2)SO_2OH$
Nitric acid	NO_2OH
Sulphuric acid	$SO_2(OH)_2$
Carbonic acid	$CO(OH)_2$
Cyanic acid	CNOH
Picric acid	$C_6H_2(NO_2)_3OH$
Orthosilicic acid	$Si(OH)_4$
ilicic anhydride	SiO_2

Aquo Bases and Basic Oxides.

odium hydroxide	NaOH
thium hydroxide	LiOH
Lithium oxide	Li_2O
Calcium hydroxide	$Ca(OH)_2$
Magnesium oxide	MgO
Mercuric oxide	HgO
Bismuth oxide	Bi_2O_3

Aquo Salts.

Potassium acetate	CH_3COOK
Magnesium acetate	$(CH_3COO)_2Mg$
Potassium benzenesulphonate	$C_6H_5SO_2OK$
Potassium sulphate	$KOSO_2OK$
Potassium acid sulphate	$HOSO_2OK$
Potassium carbonate	KOCOOK
Potassium acid carbonate	HOCOOK
Mercuric succinate	
Isatin silver (Peters, *Ber.*, 1907, xl., 235)	
Mercury cyanurate (Hantzsch, *Ber.*, 1902, xxxv., 2717)	$(CN)_3(OHg)_3$

Amphoteric Hydroxides.

Zinc hydroxide	$Zn(OH)_2$
Lead hydroxide	$Pb(OH)_2$

I. THE AMMONIA OR NITROGEN SYSTEM.

Ammono Acids and Acid Nitrides.

Acetamide	CH_3CONH_2
Diacetamide	$(CH_3CO)_2NH$
Triacetamide	$(CH_3CO)_3N$
Benzamide	$C_6H_5CONH_2$
Benzenesulphonamide	$C_6H_5SO_2NH_2$
Nitrobenzenesulphonamide	$C_6H_4(NO_2)SO_2NH_2$
Nitramide	NO_2NH_2
Sulphamide	$SO_2(NH_2)_2$
Sulphimide	$(SO_2NH)_3$
Carbamide	$CO(NH_2)_2$
Nitrourea	$NH_2CONH(NO_2)$
Guanidine	$HNC(NH_2)_2$
Nitroguanidine	$NH_2C(NH)NHNO_2$
Parabanic acid	$C_3O_3(NH)_2$
Uric acid	$C_5O_3(NH)_4$
Cyanoamide	$CNNH_2$
Picramide	$C_6H_2(NO_2)_3NH_2$
Silicon amide	$Si(NH_2)_4$
Silicon imide	$Si(NH)_2$
Silicon nitride	Si_3N_4

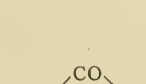
II.

Ammono Bases and Basic Nitrides.

Sodium amide	$NaNH_2$
Lithium amide	$LiNH_2$
Lithium imide	Li_2NH
Lithium nitride	Li_3N
Calcium amide	$Ca(NH_2)_2$
Magnesium nitride	Mg_3N_2
Mercuric nitride	Hg_3N_2
Bismuth nitride	BiN

III.

Ammono Salts.

Monopotassium acetamide	CH_3CONHK
Dipotassium acetamide	CH_3CONK_2
Sodium diacetamide	$(CH_3CO)_2NNa$
Magnesium acetamide	$(CH_3CONH)_2Mg$
Monopotassium benzenesulphonamide	$C_6H_5SO_2NHK$
Dipotassium benzenesulphonamide	$C_6H_5SO_2NK_2$
Dipotassium sulphamide	$KHNSO_2NHK$
Monopotassium sulphamide	H_2NSO_2NHK
Dipotassium urea	KHNCONHK
Monopotassium urea	$H_2NCONHK$
Potassium nitrourea	$H_2NCONKNO_2$
Potassium nitroguanidine	$H_2NC(NH)NKNO_2$
Mercuric succinamide	
Mercuric succinimide	
Silver succinimide	
Isatin mercury (Peters, *Ber.*, 1907, xl., 235)	
Potassium parabanate	$C_3O_3(NH)(NK)$
Calcium cyanoamide	CNNCa
Mercuric isocyanurate (Hantzsch, *Ber.*, 1902, xxxv., 2717)	$(CO)_3(NHg)_3$

IV.

Amphoteric Amides, Imides, and Nitrides.

Zinc amide	$Zn(NH_2)_2$
Silver amide	$AgNH_2$
Lead imide	PbNH
Cuprous nitride	Cu_3N
Thallium nitride	Tl_3N

The Water or Oxygen System.

Salts of Amphoteric Hydroxides.

Potassium zincate	—
Potassium plumbite	—
Potassium stannate	$KOSnOOK.3H_2O$

Aquobasic Salts.

Basic mercuric fluoride	$HgOHgFl_2.H_2O$
Basic mercuric chlorides	$Hg_xO_yCl_z$
Basic mercuric bromide	$Hg_4O_3Br_2$
Basic lead iodides	$xPbI_2.yPbO$

V.

The Ammonia or Nitrogen System.

Salts of Amphoteric Amides and Imides.

Potassium ammonozincate	$KHNZnNKH.2NH_3$
Potassium ammonoplumbite	$PbNK.2\frac{1}{2}NH_3$
Potassium ammonostannate	$KNSnNK.4NH_3$ or $K_2Sn(NH)_3.3NH_3$

VI.

Ammonobasic Salts.

Basic mercuric chlorides	NH_2HgCl $NH_2HgCl.HgCl_2$ $(Hg_2NCl)_2.HgCl_2$
Basic mercuric bromides	NH_2HgBr $(Hg_2NBr)_4.HgBr_2$ $NH(HgBr)_2$ Hg_2NBr
Basic lead iodide	$Pb_2NI.2NH_3$

Since it will be frequently necessary in the course of this article to speak of the acids, bases, and salts of this system and to describe a considerable number of reactions between these ammonia derivatives, it becomes desirable to formulate a scheme of nomenclature in order that the discussions which follow may be carried on as clearly and concisely as possible. A brief statement of the system of nomenclature which will be used is given herewith.

1. The author has already proposed (*Journ. Am. Chem. Soc.*, 1905, xxvii., 823) to designate the acids, bases, and salts of the ammonia or nitrogen system as *ammono acids*, *ammono bases*, and *ammono salts* respectively, which is to say that the acid amides and imides, including the amides and imides of the non-metallic elements, are ammono acids, the metallic amides and imides are ammono bases, and the metallic derivatives of the acid amides and imides are ammono salts (Note 4).

2. When it becomes desirable to distinguish between the acids, bases, and salts of the ammonia system, on the one hand, and those of the oxygen or water system on the other, it will be convenient to refer to the members of the latter system as *aquo acids*, *aquo bases*, and *aquo salts* (Note 5).

3. We shall find that compounds exist which are related to ammonia as the ordinary acid salts and basic salts—that is to say, the aquoacid salts and the aquobasic salts—are related to water. Such compounds will be called ammonoacid salts and ammonobasic salts respectively (Note 6), and the process whereby the ammonobasic salts are formed will be called *ammonolysis*. It will be shown that ammonolytic reactions take place in liquid ammonia solutions in a manner entirely analogous to the familiar hydrolytic reactions in water solutions.

4. We shall also have occasion to speak of compounds which are related to ammonia as the ordinary hydrated salts, or salts with water of crystallisation, are related to water. Obviously such compounds may very properly be called *ammonates*, just as salts with water of crystallisation are sometimes called hydrates, or they may be called either *ammonated salts* or *salts with ammonia of crystallisation*. (These designations have frequently been used by others).

5. Furthermore, when it becomes desirable to emphasise the distinction between a water-free salt and a salt with water of crystallisation or containing adsorbed water, the former is usually referred to as the anhydrous salt. Similarly, when it is desired to speak of ammonia-free salts, in contradistinction to a salt containing ammonia, either adsorbed or as ammonia of crystallisation, it will be convenient to speak of the former as *deammonated salts* or as *anammonous salts*. (A designation first used in print by Browne and Houlehan, *Science*, 1911, xxxiv., 284).

6. The relationship which the bases of the water system bear to the metallic oxides, on the one hand, and those which the acids bear to their anyhdrides on the other, are found to be exemplified by the relationship which exists between the acid amides and imides and the nitrides of the non-metallic elements or electronegative radicals, and between the metallic or basic amides and imides and the metallic nitrides. We shall therefore on occasion refer to the non-metallic nitrides as *acid nitrides*, or *acid anammonides*, and to the metallic nitrides as *basic nitrides*.

7. Finally, as there are amphoteric hydroxides and oxides, so we shall find it convenient to speak of those ammonia derivatives which show amphoteric properties as *amphoteric amides*, *imides*, and *nitrides*.

In the accompanying tables is given a selected list of compounds belonging to the water and ammonia systems respectively.

Notes.

4. Acetamide and diacetamide are accordingly ammonoacetic acids; the potassium derivatives of acetamide and sodium diacetamide are ammonoacetates of potassium and sodium respectively. Urea is ammonocarbonic acid and the potassium derivatives of urea obtained by Franklin and Stafford are potassium ammonocarbonates. Trinitroaniline is ammonopicric acid. Calcium cyanamide is the calcium salt of ammonocyanic acid.

5. The writer in another place (*loc. cit.*) has proposed the prefix hydro for the oxygen acids, bases, and salts, but submits that the word aquo, which he encountered in the writings of Werner ("Neuere Auschauungen auf dem Gebiete der anorganischen Chemie") is a much better designation. The generally accepted practice of referring to the aquo acids, bases, and salts as oxygen acids, bases, and salts would require us to designate the analogous derivatives of ammonia as nitrogen acids, bases, and salts, a procedure which is open to obvious objections.

6. Not basic ammono salts and acid ammono salts. The formulæ for three ammono basic salts are NH_2HgCl, NH_2HgNO_3, and $NH_2HgNH(CH_3CO)$; the first formula represents an ammonobasic halogen salt, the well-known infusible white precipitate; the second represents an ammonobasic aquo salt, a compound which has been recently prepared (Strömholm, *Zeit. Anorg. Chem.*, 1908, lvii., 72), and the third represents an ammonobasic ammono salt, a compound not known to exist but which may possibly be prepared by the action of potassium amide on acetamide mercury. An ammono salt may be expected to undergo either ammonolysis to form an ammonobasic ammono salt, such as represented by the last formula above, or hydrolysis to form an aquobasic ammono salt, such as represented by the formula $HCONHHgOH$, a compound which has been prepared by Fischer and Grützner (*Arch. Pharm.*, 1894, ccxxxii., 329).

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Protection of Nature's Fauna.

As president of the French delegation at the International Conference of Berne for the protection of nature's fauna, M. Edmond Perrier, director of the Natural History Museum, has communicated to the Academy of Sciences the principal decisions taken at the conference. M. Perrier recalls the fact that, unless a protective legislation be adopted by different countries, several species of animals will soon disappear. Thus, the large cetacea, such as the whale and cachalot, hunted excessively, especially by the Norwegian fishing societies, are doomed to rapid destruction. In ten years the rhinoceros and African elephants will also have disappeared unless the African hunting is put under control. The birds of paradise that are confined to New Guinea, a country not so large as England, and to the Solomon Islands, the extent of which is inferior to that of Corsica, are being veritably massacred. The aigrettes are undergoing the same fate. In presence of these facts, the conference under the presidency of M. Forrer, a Swiss federal councillor, has decided to name a permanent international committee, which will hold its sittings at Bale, and will meet at least once every three years. Each country adhering to the conference will be represented by at least two delegates. Each delegate will submit to their Government the proposals of the committee destined to bring about legislative measures in view of the efficacious protection of animals. Answering to a question of the secretary of the Academy, M. Darboux, M. Perrier added that the feather industry is trying to hinder all protective legislation. At the present time more than 50,000 workpeople are employed in plucking the skins of aigrettes, birds of paradise, and other birds. A feather worker earns about 4 francs a day to pluck 400 aigrettes. In face of the disappearance of aigrettes a feather merchant has appointed the Natural History Museum to award a prize of £400 to any one who succeeds in the breeding of these birds. But it is hardly probable that the prize can be awarded in the limits appointed by the giver. From all accounts it appears that the feather industry is very prosperous, while, on the other hand, there are at present 30,000 artificial flower makers in Paris without work. The feather has killed the flower.

Mercury and Musts.

The influence of mercury on alcoholic fermentation has just been studied by M. P. Nottin. The presence of mercury in a liquid in a state of fermentation produces two distinct phenomena. The mercury feebly attacked by the natural acid must produce toxic salts, which, according to their dose, keep back or hinder entirely the development of the yeast. Secondly, the mercury as a metal increases the production of the yeast, because it continually removes from the must its carbonic acid by a phenomenon of a purely physical order, and thus allows the yeast to breathe and vegetate more easily. Platinum and porous substances produce the same effect.

Autumn Leaves.

The sumptuous gold and purple attire with which the autumn forests are bedecked has, for a very long time, puzzled numbers of learned men. Many physiologists have wondered what is the nature of this coloration. Prof. Gaston Bonnier has explained, before the Academy of Sciences the researches of M. Raoul Combes, who has been able to realise the production of the red substance of leaves outside the organism itself. Another scholar, M. Guilliermons, has studied the manner in which this red substance is produced from a histological point of view. The substance is produced by misochondries, those little living elements that are in the interior of all celulles. M. Raoul Combes has also shown that there exists in green leaves a yellowish substance, which he has isolated and crystallised, and it is this substance he has transformed into a red substance having identically the same point of fusion and the same properties as that which is extracted from reddened leaves. Now, it was supposed that this transformation took place under the influence of oxidation, but the proof was never given. M. Raoul Combes has shown that the contrary is the fact. It is by induction that the red substance is obtained at the expense of the yellowish substance of green leaves. It is easy to understand the importance of this question, for these researches are doubtless applicable to the coloration of all pink, violet, red, lilac, or blue flowers.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 27th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*Method of Measuring the Pressure produced in the Detonation of High Explosives or by the Impact of Bullets.*" By Prof. B. Hopkinson, F.R.S.

A steel shaft about 1¼ inches diameter and 4 feet long is suspended horizontally from strings so that it can swing in a vertical plane as a ballistic pendulum. At one end it carries an end-piece of the same diameter and several inches long. The end-piece is held on by magnetic attraction; the surfaces of the joint are carefully faced. If a bullet be fired at the other end a wave of pressure travels along the shaft, whose length represents the duration of the blow on the scale 1 inch = 5×10^{-6} second approx. The wave passes the joint without change, and is reflected as a tension-wave from the free end. If length of wave exceeds twice that of end-piece, the tail of pressure-wave will have passed the joint when the head of tension-wave reaches it, and the piece will fly off, having trapped within it the whole momentum of the blow, leaving the shaft at rest.

By experimenting with different lengths of end-piece and finding that which is just long enough to stop the shaft, the duration of blow can be determined. The end-piece is caught in a ballistic pendulum and its momentum measured; thus, knowing the time, the average pressure is determined. By using shorter pieces and finding the percentage of total momentum trapped in each the maximum pressure exerted during blow can also be found.

Applied to investigation of the blow given hy a lead bullet, the method gave results in close accord with those expected on the assumption that the bullet behaves as though it were liquid, the measured duration of blow being nearly that required by the bullet to travel its own length.

Measurements by the same method of pressures produced by detonation of a 1 oz. dry gun-cotton primer showed that, at a distance of ¾ inch from surface of cotton, the pressure is practically all gone in 1/50,000 second, the average pressure during that period being about 25 tons per square inch, and the maximum of the order of 45 tons per square inch. At surface of cotton the duration of blow is probably about the same and pressures roughly twice as great.

The bearing of these results on shattering of ductile steel plates by detonation of gun-cotton in contact with them is considered.

"*Gravitational Instability and the Nebular Hypothesis.*" By J. H. Jeans, F.R S.

The work of Maclaurin, Jacobi, Poincaré, and Darwin on rotating fluids has applied only to the abstract case in which the mass is considered perfectly incompressible and homogeneous. To estimate the bearing of their results on astronomical problems, it is important to know to what extent these results remain valid for actual compressible heterogeneous masses.

The result of the present investigation can be summed up very concisely by saying that the ideal mass of incompressible fluid has been found to supply a surprisingly good model by which to study the behaviour of the more com-

plicated natural systems considered in astronomy. The systems considered in the present paper are those in which the pressure p is a function of the density ρ, the special case in which the relation between p and ρ is given by Laplace's law $p = c(\rho^2 - \sigma^2)$, and systems in which the matter, when free from rotation, is arranged in spherical layers, such that Laplace's law is obeyed in each layer, but the constants of the law vary from layer to layer. The problem especially under consideration has been that of determining the amount of rotation at which configuration of revolution (*e.g.*, spheroids) first become unstable. In so far as it has been found possible to examine this question, it has been found that, without exception, the compressible mass will behave up to this point in a manner almost exactly similar to the incompressible mass, and results, both qualitative and quantitative, obtained for the latter, will be true for the former. The compressible mass, set into rotation, will apparently pass through a series of stable flattened figures very similar to the Maclaurin spheroids. It will then for just about the same amount of rotation as the incompressible mass (rotation being measured by $\omega^2 \div$ [mean density]) leave the symmetrical form and assume a series of forms similar to the Jacobian ellipsoids. The main result appears to suggest that the work of Poincaré and Darwin is applicable to the bodies of nature and not merely to mathematical abstractions.

"*Diffraction of Light by Particles comparable with the Wave-length.*" By B. A. Keen, B.Sc., and A. W. Porter, F.R.S.

A suspension of finely-divided sulphur, obtained by precipitation from a solution of thiosulphate of soda by the addition of acid, ordinarily diffracts an excess of blue light, so that a white source of light seen through it looks red. One of us discovered that if the particles be allowed to grow the red image gradually changes over in colour, becoming at one stage a deep indigo blue, and afterwards passing through various shades of green to white.

The present investigation was undertaken to obtain quantitative information in regard to this phenomenon. Measurements of the intensity of the directly transmitted light were made for different colours by means of a Höfner spectrophotometer. The data obtained showed that for any particular colour the transmitted light diminishes up to a certain stage and then increases. The time in which the minimum intensity is reached is nearly proportional to the wave-length. Observations with a microscope showed that the size of particle for which the minimum occurs is from four to six times the wave-length. These are considerably larger than those examined theoretically by Lord Rayleigh. Some physico-chemical considerations are introduced in an attempt to connect the diameter with the time. The data are published with the object of attracting mathematicians to an interesting but difficult region of the subject of diffraction.

"*Colour of Zircons, and its Radio-active Origin.*" By Prof. R. J. Strutt, F.R.S.

"*Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-Ray Spectrometer.*" By Prof. W. H. Bragg, F.R.S.

The energy of the pencil of X-rays which falls on the crystal of the X-ray spectrometer is in part spent within the crystal through absorption, which implies the production of cathode and characteristic X-rays, and in part is scattered, producing the reflected ray when circumstances are favourable. It is found that where there is much absorption there is little reflection.

It is known from Barkla's work that absorption coefficients show sharp discontinuities. Copper, for example, is relatively transparent to its own characteristic radiation, and to a lesser degree to the radiations of all substances of less atomic weight than its own. It is relatively opaque to the radiations of heavier atoms. Consequently, a copper screen placed across the path of the rays in the spectrometer reduces the intensities of the shorter waves far more than the intensities of the longer, the critical value being sharply defined. This is illustrated by an examination of the spectra of Os, Ir, Pt, Pd, Rh, Cu, and Ni, and of the effects of various screens.

The same effect is found to occur when the absorbing atom is within the crystal. Zinc blende gives a spectrum in which the A peak of Pt is very exceptionally strong in comparison with the rest of the spectrum, because zinc is relatively opaque to all shorter waves. Sodium arsenate gives a spectrum in which both the A and the B peaks are strong. There is no obvious resonance of any atom in the crystal to incident rays.

This implies that the scattering power does not show the same discontinuities as the absorption coefficients. There is, in fact, good evidence that the scattering power is proportional to the atomic weight. The reflecting power of a plane in the crystal depends on the sum of the weights of the atoms it contains and not on their nature. For instance, the alternate (100) planes of CaF_2 are equally effective, though they contain only Ca, and only F atoms alternately, because the atomic weight of Ca is nearly twice that of F.

The best reflectors are therefore those crystals of which the absorption coefficients are smallest in comparison with their weights or their scattering powers. For this reason alone the diamond must be a very good reflector.

"*Analysis of Crystals by the X-Ray Spectrometer.*" By W. L. Bragg.

The paper contains the results of the examination of various crystals by the X-ray spectrometer. The rays from bulbs with anti-cathodes of palladium or rhodium were used, as each of these metals gives off radiation consisting almost entirely of a single monochromatic component. By a quantitative comparison of the intensities of the successive orders of reflection by various crystal faces, it is shown that the X-ray spectrometer can be made to give a very complete analysis of the crystal structure. For instance, in the case of iron pyrites it is possible to find the relative positions of the interpenetrating lattices on which the iron and sulphur atoms are placed, to within 2 per cent of the distance between neighbouring points of the same lattice.

The structures particularly investigated in the paper are those of the isomorphous sulphides, pyrites, and hauerite, and of the series of compounds which compose the calcite family of minerals. By a study of these last compounds, it is concluded that the diffracting power of an atom is proportional to its atomic weight.

"*Ship Resistance: The Wave-making Properties of certain Travelling Pressure Disturbances.*" By T. H. Havelock, D.Sc.

The paper contains a theoretical comparison of the wave-making resistance associated with certain distributions of surface pressure. Various inferences are drawn in regard to variation of resistance with speed, and the speeds at which typical interference effects occur. In particular, types are examined which are similar in general form to those associated with the motion of ship models in recent work at the William Froude tank in the National Physical Laboratory.

"*Mathematical Representation of a Light Pulse.*" By R. A. Houstoun, D.Sc.

The object of this paper is to call attention to a new series of expressions representing the initial form and dispersion of a light pulse. They have been suggested by one of Kelvin's hydrodynamical papers, and are derived from his instantaneous-plane-source solution in the conduction of heat.

For $t = 0$ they give sharp symmetrical maxima descending to 0 within a short distance from the origin, and for t large they give well-defined groups of waves, in which the wave-length decreases from the front to the rear of the group.

The energy distribution of one of the groups obeys Wien's law for black-body radiation, and allows the height of the initial pulse in this case to be interpreted very simply in terms of the temperature.

CHEMICAL SOCIETY.

(Continued from p. 280).

244. "*Note on the Structure of certain Lactones formed by the Fission of the* gem.-*Dimethyl*cyclo*propane Ring.*" By WILLIAM HENRY PERKIN, jun., and JOCELYN FIELD THORPE. (*Trans.*, 1913, 1760).

The constitution of the lactone-dicarboxylic acids A and B described in a former paper (*Trans.*, 1901, lxxix., 764) and of lactone-dicarboxylic acids prepared by Baeyer (*Ber.*, 1896, xxix., 2792) and by Aschan (*Annalen*, 1913, cccxcviii., 299) is discussed.

245. "*The Resolution of* 2 : 3-*Diphenyl*-2 : 3-*dihydro*-1 : 3 : 4 *naphthaisotriazine into Optically Active Components.*" By WILLIAM JACKSON POPE and CLARA MILLICENT TAYLOR. (*Trans.*, 1913, 1763).

The resolution of this base is effected by crystallisation with *d*-bromocamphor-π-sulphonic acid; the fractional crystallisation of the mixed salt which results yields two salts of the optically active acid, containing the *d*- and the *l*-base respectively. The liberation of the optically active base from the salts is accompanied by its complete optical inversion.

246. "*The Mutual Solubilities of Ethyl Acetate and Water and the Densities of Mixtures of Ethyl Acetate and Ethyl Alcohol.*" By RICHARD WILLIAM MERRIMAN. (*Trans.*, 1913, 1774).

The mutual solubilities of ethyl acetate and water have been determined by a method which enables a test of the accuracy of the results to be applied. Although contraction occurs in the formation of both of the saturated solutions, yet the solubility of ethyl acetate in water increases with rise of temperature, but the solubility of water in ethyl acetate decreases with rise of temperature. There is no point of maximum density of water saturated with ethyl acetate above 0°.

When alcohol is mixed with ethyl acetate a small expansion takes place; the maximum percentage expansion occurs when the two liquids are approximately in equimolecular proportions. A table of densities of mixtures of the two liquids is given.

247. "*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures above and below the Atmospheric Pressure.*" Part I. By RICHARD WILLIAM MERRIMAN. (*Trans.*, 1913, 1790).

The change in composition of the azeotropic mixture of ethyl acetate and water has been traced from 25 mm. to 1500 mm. pressure. The percentage of water increases continuously with the pressure, and there is no evidence of a constant value being reached at higher pressures. Assuming that the expression $p_1/p_2 = x/(1-x)$, where p_1 and p_2 are the partial pressures and x and $(1-x)$ are the molecular proportions of the two substances, holds for the azeotropic mixture, the partial pressure of the water has been calculated. At all temperatures this partial pressure is almost exactly equal to the vapour pressure of pure water at the same temperature. The Duhem-Regnault law, which states that in the case of partly miscible liquids the total pressure of the heterogeneous mixture is equal to the vapour pressure of the more volatile component in the pure condition, has been found to be erroneous.

248. "*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures above and below the Atmospheric Pressure.*" Part II. By RICHARD WILLIAM MERRIMAN. (*Trans.*, 1913, 1801).

The alterations in composition of the ester-alcohol binary mixture and the ternary mixture have been studied at pressures ranging from 25 mm. to 1500 mm. There is no evidence of constant composition being attained at any pressure.

Although the vapour-pressure curves of ethyl alcohol and ethyl acetate cross at a pressure of 948 mm., yet the percentage of alcohol in the azeotropic mixture increases continuously with the pressure, and shows no break at the point of crossing of the vapour-pressure curves. The following general rule for the change of composition of a binary azeotropic mixture of minimum boiling point has been deduced from the present investigation:—The percentage of the liquid, for which dp/dt is the smaller, increases as the pressure decreases. The rule is followed in seven different cases. The only exception that has been found is the ethyl alcohol-water mixture (Wade and Merriman, *Trans.*, 1911, xcix., 997).

249. "*The Mechanism of the Condensation of Glucose with Acetone.*" By JAMES LESLIE AULD MACDONALD.

Experience in the preparation of glucose-monoacetone and diacetone has shown that, however prolonged the treatment with acid acetone may be, glucose-monoacetone may always be isolated at the end of the reaction, and, moreover, the two condensation products are obtained in very variable yields. The conclusion is drawn that the formation of these compounds does not depend on the hydrolysis of glucose dimethylacetal, followed by condensation in definite stages with 2 molecules of acetone.

By arresting the condensation of glucose dimethylacetal with acetone at an early stage, *glucose dimethylacetal-$\varepsilon\zeta$ monoacetone* has been isolated as the main initial product. (The nomenclature adopted is that used in *Trans.*, 1913, ciii., 564). This compound is highly unstable towards heat and acids, and readily loses methyl alcohol, with the formation of *methylglucoside-$\varepsilon\zeta$-monoacetone*. The position of the acetone residue in this compound was established by methylation by the silver oxide method, and subsequent hydrolysis of the product in two stages. In this way, *$\beta\gamma$-dimethyl methylglucoside-$\varepsilon\zeta$-monoacetone*, *$\beta\gamma$ dimethyl methylglucoside*, and lastly *$\beta\gamma$-dimethyl glucose* were obtained.

On the other hand, prolonged treatment of glucose dimethylacetalmonoacetone with acid acetone results in simultaneous hydrolysis and condensation taking place, and the formation of glucose diacetone. The di-derivative thus produced has therefore the acetone residues linked to the two pairs of carbon atoms, $\alpha\beta$ and $\varepsilon\zeta$ respectively, a conclusion which harmonises with all the evidence available regarding the structure of this compound.

The condensation reactions of glucose dimethylacetal are thus extremely complex. When left in contact with acetone containing hydrogen chloride the initial products are glucose monoacetone and glucose dimethylacetalmonoacetone, the latter compound probably furnishing the chief source of glucose diacetone.

250. "*Condensation of Acid Chlorides with the Ethyl Esters of* (a) *Cyanocetic Acid*, (b) *Malonic Acid, and* (c) *Acetoacetic Acid.*" Part I. By CHARLES WEIZMANN, HENRY STEPHEN, and GANESH SAKHARAM AGASHE. (*Trans.*, 1913, 1855).

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 103).

251. "*2-Phenyl-5-styryloxazole.*" By ROBINSON PERCY FOULDS and ROBERT ROBINSON. (*Trans.*, 1913, 1768).

In order to characterise 2-phenyl-5 styryloxazole the authors have prepared the substance by treating *styryl benzoylaminomethyl ketone* with concentrated sulphuric acid.

252. "*The Action of Sulphur Chloride and of Thionyl Chloride on Metallic Salts of Organic Acids: Preparation of Anhydrides.*" By WILLIAM SMITH DENHAM and HILDA WOODHOUSE. (*Trans.*, 1913, 1861).

The reaction between sulphur chloride and metallic salts of organic acids in the presence of an indifferent solvent, which is represented for the case of silver benzoate by the equation $2C_6H_5\cdot CO_2Ag + S_2Cl_2 = (C_6H_5\cdot CO_2)_2S_2 + 2AgCl$ (*Trans.*, 1909, xcv., 1237), has been found to be general for many types of acids. Salts of hydroxy- and amino-acids behave exceptionally. The compounds of the type $(R\cdot CO_2)_2S_2$ are in all cases unstable, and decompose spontaneously with separation of sulphur and formation o sulphur dioxide and the anhydride of the acid. Unde

similar conditions thionyl chloride usually yields sulphur dioxide, the acid anhydride, and the chloride of the metal (*Proc.*, 1909, xxv., 294), but in the case of hydroxy-acids intermediate compounds are formed, which, on loss of sulphur dioxide, give rise to anhydro-compounds. A crystalline *malic anhydride* has been prepared in this way.

The respective behaviours of sulphur chloride and thionyl chloride in these reactions are consistent with their possessing similar constitutions.

253. "*The Action of Magnesium Aryl Haloids on Glyoxal.*" By HENRY WREN and CHARLES JAMES STILL. (*Trans.*, 1913, 1770).

*iso*Hydrobenzoin, *αβ-dihydroxy-αβ-di-p-tolylethane* (m. p. 161·8—162·6°), and *αβ-dihydroxy-αβ-di-o-tolylethane* (m. p. 116·5—118°) have been prepared by the action of magnesium phenyl bromide, magnesium *p*-tolyl bromide, and magnesium *o*-tolyl bromide respectively, on unimolecular glyoxal (Harries and Temme, *Ber.*, 1907, xl., 165). In no case could definite evidence of the formation of the second theoretically possible isomeride be obtained. The *acetyl* derivatives corresponding with the two latter glycols melt at 105—106° after softening at 103—104°, and 99—100° after softening at 98·5° respectively.

254. "*The Miscibility of Solids.* Part II.. *The Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.*" By ERNEST VANSTONE. (*Trans.*, 1913, 1826).

The method of thermal analysis has been applied to binary mixtures of the type Phα3Ph.

Pascal and Norman (*Bull. Soc. Chim.*, 1913, [4], xiii., 151, 201) have shown that dibenzyl, stilbene, tolane, azobenzene, and hydrazobenzene are miscible in all proportions in the solid state; also that with benzylaniline, benzylideneaniline, and phenyl benzyl ether eutectic diagrams are obtained, and solid-solution formation is limited.

A series of thermal diagrams for benzoin and benzil with these substances has been determined. In each case the diagram shows a single eutectic point and limited formation of solid solutions.

The eutectic point depends on the melting-points of the constituents. It is always found nearer the substance of lower melting-point. The molecular volumes at the temperatures of their melting-points of ten substances have been determined. Substances containing oxygen have the greatest molecular volumes.

The exceptional behaviour of benzil, when compared with other symmetrical compounds of the type PhαβPh, is discussed, and the greater molecular domain of benzil is suggested as the cause of its lower degree of miscibility.

255. *The Solubilities of Alkali Haloids in Methyl, Ethyl, Propyl, and* iso*Amyl Alcohols.*" By WILLIAM ERNEST STEPHEN TURNER and CRELLYN COLGRAVE BISSETT.

The solubilities, in methyl, ethyl, propyl, and *iso*amyl alcohols, of lithium chloride and iodide, sodium chloride and iodide, potassium chloride, bromide, and iodide, and rubidium chloride have been determined. Measurements were made at a common temperature of 25°, and in the case of lithium chloride in ethyl alcohol, also over the range from 0° to 60°.

The existence of the compound $LiCl,4C_2H_6O$, first indicated by Simon, was confirmed, and its transition-point into lithium chloride fixed at 17·4°. A compound $LiI,4C_3H_8O$, stable at 25°, was also found, and another, $NaI,3CH_4O$, stable at 15—16°.

The solubilities at 25° proved that solvent action, on the above salts, decreases continuously in passing from water through the series of alcohols; that the order of solubility is iodide>bromide>chloride, and that, in all the solvents, the solubility of the alkali chlorides is in the order:—Lithium chloride>sodium chloride>rubidium chloride>potassium chloride.

256. "*Nitration of* 1-*Chloro*-2 : 4-*dinitronaphthalene.*" By MAX RINDL.

A solution of 1-chloro-2 : 4-dinitronaphthalene in cold concentrated nitric acid deposits on keeping prismatic crystals of 1-*chloro*-2 : 4 : 5-*trinitronaphthalene*, melting at 143—144°. After several weeks 1-*chloro*-2 : 4 : 8-*trinitronaphthalene* begins to be deposited, along with the 1-chloro-2 : 4 : 5-trinitronaphthalene. The chlorine atom in both of these compounds is mobile. By treatment with aqueous solutions of alkali hydroxides they are converted into the corresponding trinitronaphthols. Only the 2 : 4 : 5-trinitro-α-naphthol can be reconverted into the corresponding chlorotrinitronaphthalene by means of *p*-toluenesulphonyl chloride and diethylaniline. Other reactions depending on the mobility of the chlorine atom are the formation of 2 : 4 : 5-*trinitro-α-naphthyl methyl ether* and of amines, for example, 2 : 4 : 5-*trinitro-α-naphthylamine*, as well as mono- and di-substituted alkyl and aryl amines. Copper powder removes the chlorine, and two molecules join together, forming dinaphthyl derivatives. In the case of 1-chloro-2 : 4 : 5-trinitronaphthalene a secondary reaction takes place, resulting in the elimination of chlorine and its replacement by hydrogen, with the formation of 1 : 3 : 8-trinitronaphthalene.

257. "*The Decomposition of Carbamide.*" By GEORGE JOSEPH BURROWS and CHARLES EDWARD FAWSITT.

Previous investigations on the decomposition of carbamide in aqueous solutions by one of the authors (*Zeit. Phys. Chem.*, 1902, xli., 603) have been extended to solutions in aqueous alcohol.

Addition of alcohol decreases the velocity of decomposition, but does not alter the mechanism of the reaction, which is a unimolecular one.

The theory already put forward that carbamide is not hydrolysed by water or aqueous solutions of acids is confirmed.

Carbamide decomposes primarily into ammonium cyanate, and is then decomposed into carbonate.

The authors believe that the decomposition of carbamide is the first chemical reaction to be investigated (1902), the mechanism of which demands the assumption of intermediate products, the existence of which has been proved.

258. "*The Viscosity of Sugar Solutions.*" By CHARLES WILFRED ROBERTS POWELL.

The results of an investigation into the viscosities of aqueous solutions of sucrose, dextrose, and lævulose are given, dealing first with simple solutions containing only one of the sugars, and then with complex solutions containing mixtures of them.

The effect of temperature on the viscosity of these solutions is found to be well expressed by Poiseuille's equation—

$$\eta t = \frac{\eta_0}{1 + at + \beta t^2},$$

where η_0 is the viscosity at 0°, ηt is the viscosity at t°, and α and β are constants. If the concentration of the solution is expressed as grms. of solute per grms. of solvent, the relation between viscosity and concentration is a logarithmic one, and may be represented by the equation $\eta x = A^x$, where x is the concentration and A a constant.

A new method of calculation of the viscosity of simple solutions is discussed, the time of flow of each of the constituents of the solution being calculated. By this means it is thought possible to examine the change in viscosity of the solute in concentrating solutions, as distinct from the change in viscosity of the solution.

A possible explanation of the deviation of the increase in viscosity of solutions with increasing concentration from any simple law is outlined. The theory given does not attempt to explain fully the question of viscosity, but indicates how the friction between different groups of molecules in the solution may definitely characterise the order of the change in viscosity with change in the composition of the solution.

It was found that for aqueous solutions of the three sugars mentioned, the two equations—

$$\eta x = Ax ,$$

$$\eta = \frac{m\eta^a + n\eta b}{(m + n)}$$

may be used conjointly with a fair degree of accuracy to calculate the viscosity of a solution containing two or more of the sugars.

259. "*The Rate of Hydration of Acid Anhydrides: Acetic, Propionic, Butyric, and Benzoic.*" By Bernard Howell Wilsdon and Nevil Vincent Sidgwick.

The velocity of this change was measured by Rivett and Sidgwick's method (*Trans.*, 1910, xcvii., 732) by observing the rise in conductivity of the solution.

The conductivity of acetic acid was measured at 18°, of propionic at 18° and 25°, and of butyric at 25°. Approximately constant values of the dissociation constant are obtained in dilute solution if the conductivity of the water used is added to that of the solution.

The rate of hydration of the corresponding anhydrides was measured at the same temperatures, and also that of benzoic anhydride at 25°. The velocity of change of acetic anhydride is about twice that of propionic, about four times that of butyric, and about eight times that of benzoic.

With acetic anhydride at 18°, as was previously observed by Rivett and Sidgwick at 25°, the velocity decreases steadily with increase of concentration above about 0·2N; the same occurs with propionic anhydride above about 0·02N. The correction for the diminution in the concentration of the water only accounts for a small part of this fall. If, however, the activities of the two reacting molecules (water and anhydride) are assumed to be proportional to the fluidity of the solution, and the observed velocities are multiplied by the square of the viscosity, the results are found to be constant (for both anhydrides and at both temperatures) within the limits of experimental error.

Monochloroacetic anhydride was found to be hydrated with a velocity too great for measurement—at least one hundred and fifty times that of acetic anhydride.

260. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution.* Part IV. *The Rotatory Powers of the Secondary Alcohols of the Formula* $C_2H_5{\cdot}CH(OH){\cdot}R$." By Robert Howson Pickard and Joseph Kenyon.

A description is given of the synthesis and resolution of thirteen alcohols of the series $C_2H_5{\cdot}CH(OH){\cdot}R$. These optically active carbinols have been examined polarimetrically in the homogeneous state, and in alcoholic and in benzene solution. The results show that, whilst the molecular rotatory powers gradually increase as the series is ascended, there are further exaltations when the growing chain contains about five and about ten carbon atoms. It has been shown also that a similar effect on the molecular rotatory powers of the series $CH_3{\cdot}CH(OH){\cdot}R$ is only noticeable when these are determined in solution, as in the homogeneous state the molecular rotatory powers of the carbinols of this series increase regularly with the mass of the compounds.

The optical rotatory dispersive power of the higher members of the series is a constant, and is independent of the temperature (from 20° to 160°).

PHYSICAL SOCIETY.

Ordinary Meeting, November 14th, 1913.

Prof. C. H. Lees, Vice-President, in the Chair.

A paper entitled "*On the Thermal Conductivity of Mercury by the Impressed Velocity Method*," by H. Redmayne Nettleton, B.Sc., was read by Dr. A. Griffiths.

The paper gave an account of the determination of the thermal conductivity of mercury at the ordinary temperature of the room by the impressed velocity method first described by the author in the *Proceedings* of this Society, vol. xxii., 1910. The mercury is contained within a vacuum jacketed syphon tube about 17 sq. cm. in cross-section, which is heated at the top and maintained ice-cold at its lower extremity. The distribution of temperature down this tube is determined with the aid of a single thermo-junction, while the mercury is at the same time flowing uniformly up the tube at speeds ranging from 870 to 1420 grms. per fifteen minutes. The calorimetry is thus essentially continuous flow calorimetry within the temperature gradient, the quantity of heat passing down the mercury being controlled and measured by the flow of liquid. The wires forming the thermo-elements—viz., iron and constantan—were contained within a vertical tube of 6 mm. external diameter, through the glass of which the wires were fused; this carrier tube lay within the vacuum vessel. The thermo-junction could be raised or lowered to the desired extent by a cathetometer, or could be rotated in a horizontal plane. The isothermals were found to be remarkably horizontal.

If θ_1 is the temperature at a distance L/2 above the isothermal surface at a temperature equal to that of the enclosure, and θ_2 the temperature at an equal distance below, then $\log_e \theta_1/\theta_2 = msL/2KA$, where s is the specific heat of mercury, K its thermal conductivity, A the cross-section of the tube, and m the mass of mercury crossing a section per second. Using this relationship a mean value of 0·0201 c.g.s. units at 15·5° C. is obtained for K.

The advantages of the method lie in the simplicity of the calorimetry and in the fact that temperature ratios rather than temperature differences are required.

Discussion.

Dr. C. Chree said there might be some doubt as to the exactitude with which the mathematical formulæ represented the physical facts, but the method seemed promising for determining the change with temperature of the thermal conductivity, and he inquired whether investigations had been directed towards that end. As the cross-section of the vessel appeared in the formulæ, it would give increased confidence if vessels of different section were tried and found to give accordant results.

Dr. J. A. Harker asked if the author was satisfied as to the distribution of the flow at different parts of the cross-section, and wished to know how the results compared with those of other observers.

Mr. F. E. Smith said that it appeared to him that the practice of Mr. Nettleton did not exactly tally with the conditions imposed by theory. Why did Mr. Nettleton assume that the temperature of some water in a glass tube in the proximity of the apparatus was the same as that of the outer wall of the vacuum jacket? It appeared from the data that it was not, and this being so an error was introduced, inasmuch as the isothermal taken as the "zero isothermal" was not so. If the assumed "zero isothermal" was appreciably higher than the true one the deduced thermal conductivity would be too high. Again, theory imposed a condition on the outer wall of the vacuum jacket; it must be of uniform temperature. Was this so in practice? One end of the jacket was practically at 0° C. and the other at 100° C.; there must be a temperature gradient. He would suggest that the outer wall of the vacuum jacket be cooled with circulating water in which the second thermo-junction was immersed. The beauty of Mr. Nettleton's method was apparent to all, and he trusted he would continue his experiments.

Dr. A. Russell regretted that the author, following the usual custom, called the law for the cooling of a body by radiation Newton's law, and the coefficient the Newtonian coefficient of emissivity. Newton considered the case of a block of iron being cooled by a current of air, so that the heat lost by radiation was very small compared with that lost by convection. In this case he found that the heat lost by the iron was very approximately proportional to the difference of temperature between the air and the iron. This law had been verified recently up to differences of

temperature between the cooling body and the air as high as 200° C. and 300° C. In the author's experiment, however, the tube had a vacuum jacket, so that the heat lost by convection was quite negligible. As the difference of temperature was, comparatively speaking, small, we saw by Stefan's law that the author's assumption was justifiable. In the speaker's opinion the real "Newton's law of cooling" was of great importance in practical work, and he thought that teachers and the writers of text-books ought to lay greater stress on it.

Dr. W. H. ECCLES called attention to the fact that at first sight the method would be thought to be incapable of high accuracy, because of the form of the expression for K, the conductivity. This expression had as its denominator what was practically the difference between two nearly equal magnitudes, and these magnitudes were themselves differences. That was to say, the denominator was of the nature of a second differential coefficient of an experimental curve. That such consistent results were obtained indicated remarkable precision of experiment.

Prof. LEES asked how small a difference of temperature throughout the cross-section would have been detected by the thermo-couple.

Dr. GRIFFITHS, in reply, stated that, as shown in the earlier paper, the distribution of the flow was not important, so long as the isothermals were plane.

The AUTHOR communicated the following:—In reply to the Chairman, Prof. Lees, it should be stated that a difference of temperature of 0·05° C. over a horizontal surface would easily have been detected in any position of the cathetometer. In the neighbourhood of the "zero isothermal" all resistances, except that of the galvanometer and wires, could be removed and a more delicate test made. It is safe to say that in this neighbourhood a difference of 0·02° C. would have been detected easily. Thus the isothermals are remarkably horizontal, the result far exceeding the author's expectations. Mr. F. E. Smith has raised an important point in his remarks about the "cold junction" at the temperature of the enclosure. The cold junction could not be inside the vacuum, as iron and constantan cannot be fused through glass and a vacuum of high standard maintained. An attempt to surround an earlier vacuum vessel with a glass water jacket (it is necessary to be able to see through the vacuum when adjusting the carrier-tube) resulted in its collapse, and no risks were taken with the present vessel, which is valuable, as at least ten attempts at making a third have failed. The "cold junction" was maintained in a tube under water just outside the vacuum vessel to protect it from air draughts, but on holding it in the air just outside the vacuum vessel no serious temperature difference was recorded. The vacuum, of course, was of "thermos" or X-ray standard. When the "warm junction" was in such a position as to produce no electric current the zero-isothermal was located. The author cannot doubt that the temperature of the cold junction was rightly that of the enclosure: for it stood the double test of Newton's law holding with respect to it in a statical experiment, as well as the constancy of the ratio $\log \frac{\theta_2}{-\theta_2}/L$ in many dynamical experiments. The height of the zero-isothermal varies in every experiment, being higher the faster the flow, as can be seen in the actual temperature curves given in the paper previously alluded to. Under no flow the zero was very low, being near the lower extremity of the vacuum-jacketed portion of the experimental tuba—too low, in fact, to allow of the test $\theta_1/-\theta_2=1$ over any considerable range.

A paper entitled "*Polarisation and Energy Losses in Dielectrics*" was read by Dr. A. W. ASHTON, M.I.E.E.

The object of the paper is to discuss the relations which should exist between the coefficients in Pellat's equation (as modified by Schweidler), giving the displacement in a viscous dielectric as a function of the time of charge and the P.D.

Taking the modified equation—

$$D_t = KE_0 + KE_0\Sigma\varepsilon(1-e^{-at})$$

the charging current for constant voltage becomes for $t>0$ $i_t = KE_0\Sigma\alpha\varepsilon e^{-at}$, and in the series of exponential terms α and ε can be so chosen as to make $\Sigma\alpha\varepsilon e^{-at} = \beta t^{-n}$.

The author makes the following deductions among others:—Where the polarisation current is proportional to t^{-n}, the viscous capacity of any group of molecules having the same time constant of displacement is proportional to the $(1-n)$th power of the time constant.

For values of n between 0·5 and 1·5 the maximum energy loss occurs in those groups for which a does not greatly differ from p, where $p = 2\pi\nu$.

For all positive values of n less than 2, the alternating current conductivity is proportional to the nth power of the frequency.

Experiments by Addenbrooke, Fleming and Dyke, Curtis and H. A. Wilson are quoted in support of the theoretical deductions. The paper includes a brief *résumé* of Pellat's theory.

DISCUSSION.

Dr. RUSSELL said that the author's method was ingenious, and that the formula deduced for the dielectric current agreed well with many experimental results. He thought, however, that Pellat's theory was not sound and that von Schweidler's modification of it was too elaborate to be of much practical use. He pointed out that Dr. Grover had proved that, from the mathematical point of view, Hopkinson's and von Schweidler's theories were identical. He considered that Fleming and Dyke's experimental results could not be ignored, and that none of the theories advanced up to the present explained them satisfactorily. Very different formulæ gave results which were practically identical over wide ranges, and so they were of doubtful help in enabling us to discover the causes of the phenomena. He considered that the nomenclature of dielectric theory stood badly in need of standardising. For instance, what the author called the displacement was practically the same as Maxwell's electric displacement, but Sir J. J. Thomson and several other writers called it the polarisation.

Dr. ECCLES stated that the paper compelled remark on the artificial nature of Pellat's hypothesis. This hypothesis led to an expression for the displacement current as a sum of exponential terms. Experiment required it to be a power of t, or the sum of several power terms. This required that the exponential terms of Pellat's hypothesis should be infinite in number—which deprived the hypothesis of physical meaning. It would be more logical, therefore, to begin with the power terms as fundamental, and to discard the false start given by Pellat.

Mr. ADDENBROOKE stated that in order to get at the proper theory of experiments the best dielectrics should not be used, as the effects were so minute that the chances of error were great. With poorer dielectrics, the actions were on a greater scale and easier to observe. Using an ellipsoid suspended at 45° to the electric field, he had been able to carry his experiments down to a frequency of one cycle in two hours, taking, of course, time readings of current and voltage. Dr. Ashton had not mentioned a paper by Wagner, which seemed to cover much the same ground.

Prof. C. H. LEES mentioned a later paper on the subject by Curtis, who had found that Schweidler's equations held if several terms were taken.

Dr. ASHTON, in reply, said that in Pellat's original paper there were results which showed that over a certain range the charging current could be represented by a constant times t^{-n}, and that more than one exponential term might be required. His own experiments showed that $i_t = \beta t^{-n}$ held over two or three days. The difficulty was to keep the temperature constant over a long time. Another difficulty was that if circuit were broken for a fraction of a second, the results were vitiated. In reply to Dr. Russell, he believed $i_t = \beta t^{-n}$ represented Fleming and Dyke's results better than $i_t' = a + bt$.

A paper entitled "*A Lecture Experiment to Illustrate Ionisation by Collision and to show Thermo-luminescence*" was read by Mr. F. J. Harlow.

A method of demonstrating to an audience both ionisation by collision and the reduction of the sparking potential by the presence of initial ionisation is described in the paper.

A spherical bulb, in which an electrodeless discharge is excited, contains two coils of platinum wire, coated with lime and aluminium phosphate respectively, which can be heated by means of a current. Within the range of pressure for which the electrodeless discharge can be excited, provided the discharge is not too intense, both the lime and aluminium phosphate, on being raised to incandescence, give a considerably increased effect, showing that the ions given off by these substances are effective under the action of the induced E.M.F. in producing an enormous number of others by collision.

The lower limit of the range of pressure over which the discharge can be excited with a given induced E.M.F. is considerably extended by heating either the lime or the aluminium phosphate, the former, however, being much more efficient than the latter in this respect. This extension of range is an illustration of the fact that the sparking potential is diminished by the presence of ions, and by negative ions more than by positive.

If the lime and aluminium phosphate are subjected while cold to an intense discharge for some time they exhibit the phenomenon of thermo-luminescence, the lime on being warmed gently giving out a golden yellow luminosity and the aluminium phosphate a blue. The effect with lime apparently increases with an increase of electrical activity caused by continued heating, which suggests that the thermo-luminescence and electrical activity are closely associated. This suggestion receives support from the fact that lime alone does not exhibit thermo-luminescence, and that both lime on platinum and lime on nickel, which are electrically active, do. Further experiments are being made on this point, which the author thinks will throw light on the origin of the anomalous electrical activity of lime on platinum.

A demonstration of these experiments was given.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

Extract from the Minutes of the Third Session of the Council.

At the third session of the Council of the International Association of Chemical Societies, held at the Institut Solvay, Parc Léopold, Brussels, from September 19 to 23, 1913, Prof. Haller gave an account of the negotiations which had taken place between M. Ernest Solvay and certain representatives of the International Association, and which had resulted in the offer by M. Solvay of an unconditional gift of 250,000 francs to the Association. M. Solvay further proposed to found an "International Institute of Chemistry," having for its object the facilitation of the study and progress of chemistry, without, however, excluding problems belonging to other branches of the natural sciences, provided that these have some bearing on the science of chemistry. The Institute will be governed by an "Administrative Commission" of three Belgian members (one nominated by His Majesty the King of the Belgians, a second by the University of Brussels, and a third by M. Ernest Solvay), and by a Delegation of the Council of the International Association of Chemical Societies, consisting of Messrs. Haller, Ostwald, and Ramsay. Of the Institute's annual income of from 55,000 to 56,000 francs two-thirds will be placed at the disposal of the International Association of Chemical Societies, whilst the remaining one-third will be employed in establishing scholarships for Belgian students. The Council gratefully accepted M. Solvay's offers, and further passed the following resolution: —"Ces sessions se tiendront autant que possible une fois sur deux à Bruxelles." M. Solvay has provided the International Association with offices in Brussels, where the archives will be kept, and a permanent secretary is to be appointed to take charge of them and to conduct the general business of the Association.

Prof. Haller was elected President of the Association for the ensuing year, and it was decided that the next meetings should be held in Paris some time during the first fifteen days of September, 1914.

Prof. Guye presented a report on the "Unification of Abbreviations of Titles for Scientific Journals used in Chemical Memoirs," and it was decided that, should the editors of all journals publishing chemical memoirs consider it advisable, the Council of the International Catalogue of Scientific Literature should be consulted, and a list of abbreviations should be circulated among the societies affiliated to the Association, with an invitation definitely to adopt the abbreviations for all future publications.

Prof. Werner read and explained the Report of the Commission appointed to consider the question of "the mitigation of the difficulties arising from the existing multiplicity of languages employed in scientific literature," and after prolonged discussion the Committee was reappointed to report to the next meeting of the Council, more particularly on three points:—

(*a*) The publication of an International Journal of Abstracts in three languages.

(*b*) The publication of three editions of an International Journal of Abstracts, namely, in English, French, and German.

(*c*) The publication of an International Journal containing translations into either English, French, or German of original papers appearing in the lesser known languages.

The Council received and adopted the report from the Commission for the Unification of Physico-Chemical Symbols. The following list gives some of the symbols recommended:—

Angström unit (10^{-10} metre)	Å
Density	d
Gas constant per mole	R
Mean free path	λ_f
Micron (10^{-6} metre)	μ
Millimicron (10^{-9} metre)	$\mu\mu$
Number of molecules	N
Pressure	p
Osmotic pressure	P
Van der Waal's constants	a, b
Volume (in general)	v
Volume, specific	v_s
Volume, atomic	v_a
Volume, molecular	v_m
Atomic weight and grm. atomic weight .	A
Concentration (units not specified) . ..	c
Equilibrium constant	K
Mole fraction	x
Molecular and grm. molecular weight ..	M
van 't Hoff coefficient	i
Velocity coefficient	k

The Committee received the report from the Inorganic Nomenclature Committee, and adopted the recommendations contained therein. The following symbols are adopted:—

I for iodine,
Xe for xenon,
W for wolfram,
Nb for niobium,

and Be is strongly recommended for beryllium. The Committee recommends that in indexing inorganic compounds the constituent atoms, including carbon, should be arranged in alphabetic order, making exceptions, however,

for hydrogen and oxygen, which should always be placed at the end of the formula. The recommendations of the Austrian and Russian National Committees for indicating the relative number of atoms of each element in the molecule are approved; *e.g.*, N_2O_5 becomes dinitrogen pentoxide instead of nitrogen pentoxide. In order to obtain shorter names for substances it is considered desirable to indicate the valency of the positive component by means of a suffix, the valencies one to eight being represented by the suffixes *o, a, i, e, on, an, in, en* in the order given; *e.g.*, the two chlorides of mercury would be respectively named mercuro- and mercura-chloride. It is recommended that an International Commission, composed of one member from each country represented in the Association, be appointed with Prof. Werner as chairman.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 17, October 27, 1913.

Refraction and Magnetic Rotation of Compounds with Acetylenic Function.—Ch. Moureu, P. Th. Muller, and J. Varin.—The proximity of the triple bond and of a negative (or slightly saturated radical) gives rise in the fatty series to a more or less marked exaltation of the refraction, which is greatly increased in the aromatic series by the proximity of the triple bond and the phenyl group. The rotation is qualitatively affected in the same way as the refraction (except in the case of acetylenic diacetal, which exhibits a depression). But if a table showing the relative exaltations is consulted, it is seen that the magnetic rotation is more sensitive than the refraction to the reciprocal influence of the slightly saturated radicals and the acetylenic bond. This sensitiveness is specially noticeable in the aromatic series.

Preparation of Aluminium Ethylate.—Clément Berger.—Aluminium ethylate can be prepared by the action of aluminium amalgam on absolute alcohol containing a little sodium ethylate. A small amount of sodium is dissolved in alcohol, and sheets of aluminium, amalgamated by immersion in a saturated solution of mercuric chloride, are introduced into the solution. Bubbles of hydrogen are produced, and a grey precipitate of aluminium ethylate containing a little alumina is deposited. $3C_2H_6O + Al = (C_2H_5O)_3Al + 3H$. Aluminium ethylate is very readily decomposed by water, and hence all traces of moisture must be avoided. It is decomposed by heat.

Presence of Gallium in Commercial Aluminium and its Separation.—Ch. Boulanger and J. Bardet.—Gallium appears to be very widely distributed in nature, and the spectrographic examination of many specimens of commercial aluminium always revealed its presence very distinctly. To separate it the aluminium was dissolved in HCl, and the metal always present, such as Cu, As, Sb, Sn, Pb, Zn, Fe, Na, is separated by appropriate treatment; *i.e.*, by sulphuretted hydrogen in either hydrochloric or acetic solution. After this treatment had been repeated three times only the gallium and a small amount of iron remained. Finally, treatment with boiling potash completely eliminated the iron.

Metallic Phosphides derived from P_5H_2.—R. Bossuet and L. Hackspill. By the action of liquid ammonia the alkaline phosphides, P_5M_2, are converted into crystalline ammoniacal phosphides, which are soluble in liquid ammonia. In this state they undergo double decompositions with metallic salts dissolved in the same solvent. From these reactions precipitates of phosphides are obtained of varying colour according to the metal contained in them; their general formula is P_5M, analogous to that of lead phosphide, P_5Pb, which has been analysed. All these compounds may be regarded as salts of the acid P_5H_2, which is Le Verrier's solid hydrogen phosphide.

Hydrogenation of Secondary Alcohol derived from Furfurol.—Roger Douris.—The hydrogenation of ethylfurfurylcarbinol over reduced nickel gives a mobile liquid from which the following products can be separated by fractional distillation:—(i.) Boiling-point 127—130°, under atmospheric pressure. The products are chiefly propyloxybutane and propyloxybutadiene. (ii.) Boiling-point 140—150°, under atmospheric pressure. This fraction contains dipropylketone. (iii.) Boiling-point 87—90°, under 15 mm. pressure. The principal product is ethyltetrahydrofurfurylcarbinol. (iv.) Boiling-point 110—120°, under 15 mm. pressure. This fraction is a very syrupy liquid in which there is a glycol, $C_2H_{16}O_2$.

Action of Magnesium Methyl and Ethyl Iodides on Michler's Ketone.—P. Lemoult.—When magnesium methyl iodide acts on Michler's ketone the hydrocarbon $CH_2=C(Dm)_2$ is obtained. If the liquid, which is left after all this hydrocarbon is deposited is examined, it is found to contain three compounds:—(i.) The dimer of $CH_2=C(Dm)_2$. (ii.) A compound containing 83 per cent C, 8 per cent H, 9 per cent N. (iii.) A compound containing 82 per cent C, 8 per cent H, 10 per cent N. With the ethyl compound the only product is the hydrocarbon $CH_3—CH=C(Dm)_2$.

MISCELLANEOUS.

Simple Process to Detect Nitrous Acid in presence of Nitric Acid.—A. Leclère.—An equal volume of a syrupy solution of citric acid is added to the solution to be analysed. Thus a dense liquid is obtained, and by means of a drawn-out pipette a 3 or 4 per cent solution of ammoniacal ferrous sulphate can be superposed on it. In presence of nitrous acid a brown ring appears at the surface of separation of the two liquids, while even a concentrated solution of a nitrate gives no reaction, since citric acid does not expel nitric acid from its salts. In presence of sulphides it is best to treat the solution with zinc acetate and filter off the zinc sulphide formed.

MEETINGS FOR THE WEEK.

Monday, 15th.—Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof. E. G. Coker, D.Sc.

Tuesday, 16th.—Physical, at 3 and 7. Exhibition of Physical Apparatus. "Soap Films, by L. Brennan. "Production of Vibrations on Loaded and Unloaded Strings," by J. A. Fleming.

Wednesday, 17th.—Royal Society of Arts, 8. "The Channel Tunnel," by Arthur Fell, M.P.

—— Microscopical, 8. "The Binocular Microscopes of the Past, and a New Form of the Instrument," by C. Bock.

Thursday, 18th.—Chemical, 8.30. "Chemical Examination of Sarsaparilla Root," by F. B. Power and A. H. Salway. "Aromatic Compounds obtained from the Hydroaromatic Series Part III., Bromoxylenols from Dimethyldihydroresorcin," by A. W. Crossley and N. Renouf. "Equilibrium of Dilute Hydrochloric Acid and Gelatin," by H R. Procter. "Metallic Derivatives of Acetylacetone and Acetyl-mesityl Oxide," by G. T. Morgan and H. W. Moss. "Constitution of the Ortho-diazoimines — Part IV., Isomeric Benzenesulphonyl-3:4-tolylenediazoimides" by G. T. Morgan and G. E. Scharff. "Organic Derivatives of Silicon—Part XXI., The Condensation Products of Diphenylsilicanediol," by R. Robison and F. S. Kipping. "Sorption of Gases by Celluloid," by V. Lefebure.

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THE ANALYSIS OF ILKLEY SPA WATER.

By B. A. BURRELL, F.I.C.

Modern Ilkley occupies the site of the Brigantian stronghold of Llecan, which subsequently became the Roman station of Olicana.

"Ichley Fountaine" has been in repute for bathing for about two centuries, a small bath-house having been built in 1699 ("White's Directory of the West Riding of Yorkshire," 1838, vol. ii., p. 511). Hearne's edition of Leland's Itinerary contains a letter written by Dr. Richardson in 1709 stating:—"Ilkley . . . chiefly famous for a cold well, which has done very remarkable cures in scrofulous cases by bathing, and in drinking of it."

In 1734 Dr. Short wrote:—"Ichley Spaw springs out of the middle of a Mountain, a Mile high. . . . The Water is very clear, brisk, and sparkling; has no taste, colour, nor smell different from the common Water, is of the same weight. Its Basin and Course are of no other Dye than that of a common spring. . . . Five pints of this Liquor exhaled left 7 Grains of sediment. . . . Therefore, tho' this Water is of the greatest Esteem and Repute of any in the North of England, in the King's Evil and other old Ulcers; yet it derives these effects neither from its fixt nor volatile Parts, but wholly from the Coldness and Purity of the Element."—("The Natural, Experimental, and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire, and Yorkshire," by Thomas Short, M.D., of Sheffield; London, 1734, p. 307).

Dr. Rutty, in 1757, quotes from another treatise of Short's, specifying the virtues of the "Ichley Water."—("A Methodical Synopsis of Mineral Waters," by John Rutty, M.D.; London, 1757, p. 23).

Dr. Adam Hunter's examination in 1819 gave:—Temp. of water, 48° F.; temp. in shade, 64° F.; sp. gr. at 55° F., 1·00015.

A wine gallon was found to contain:—

	Grains.
Muriate of lime	6·50
Muriate of magnesia	3·00
Total	9·50

Gaseous contents—

	Cubic inches.
Carbonic acid gas	12·60
Atmospheric air	5·40
	18·00

Quantity 100 gallons per minute, and situate nearly three-quarters of a mile from the village ("An Essay on Two Mineral Springs at Harrogate, and on the Springs at Thorp-Arch and Ilkley," by Adam Hunter, M.D.; Leeds, 1819).

T. Shaw, M.R.C.S., in 1830, states ("The History of Wharfedale"):—"The water is, perhaps, for its purity, tenuity, and coldness, the best qualified . . . of any water in this part of the country. It has been frequently analysed, but the decomposition always proved that it contains no medicinal quality, . . . it is purity and softness only, which makes it more efficacious . . . than any other water known."

There is a reference to the water in the "Spas of England—Northern Spas," vol. i., by A. B. Granville, M.D., F.R.S.; London, 1841). The author having repeatedly measured the flow, which he puts at 60 gallons a minute, the temperature being 47° F., and that of the atmosphere 55° F. The analysis of Dr. Hunter is quoted.

William West, in 1844, states that he had not analysed it, but gives its composition in grains per gallon (*Brit. Assoc. Notices*, 1845, p. 107).

Chloride of sodium	0·657
Sulphate of soda	0·366
Sulphate of lime	0·2
Carbonate of lime	2·353
Carbonate of magnesia ..	1·04
Silicate of soda	1·066
Peroxide of iron	0·060
Total	5·742

The following analysis is given in some of the local guides. The author is not stated.

	Grains per gal.	
Sulphate of sodium .	2·939	
Chloride of calcium .	0·572	
Carbonate of calcium	2·185	
Silica	1·200	
Chloride of sodium .	0·501	
Solid matter	10·796	
Free carbonic acid .	6·581	cubic inches per gal.

Temperature, 43—45° F.

For several years past the writer has taken samples of the water from the pipe used for filling the Roman bath at the White Wells, the height of which is about 660 feet above sea-level. The water issues from the middle or third grits of the millstone grit series. Variations in temperature are very slight. The following readings selected from those made on ten different occasions show the extreme variations:—

Temperature of air (shade).	Temperature of water.
16·9° C.	8·8° C.
9·4° C.	7·7° C.

The water is clear and free from sediment. The general procedure was that recommended by Fresenius, and all numbers given are the mean of at least two, and generally of three or four determinations. For substances present in minute quantity the residues obtained by the evaporation of from 45 to 50 litres of the water were used. With such quantities neither bromine, iodine, barium, or strontium could be detected. International Atomic Weights, 1912, were used for the calculations.

The constituents are as follow—

	Grms. per litre.		Grains per gal.
SiO_2	0·0152	=	1·0641
SO_4	0·0176	=	1·2368
N_2O_5	0·0001	=	0·0093
Nitrous acid	None	=	None
P_2O_5	Trace	=	Trace
Cl	0 0110	=	0·7700
Fe	0·00016	=	0·0112
Al	Trace	=	Trace
Ca	0·0169	=	1·1866
Mg	0·0090	=	0·6307
Na	0·0119	=	0·8331
K	0·00125	=	0·0876
Li	0·00019	=	0·0136
Free ammonia		=	0·0011
Albuminoid ammonia		=	0·0020
Oxygen absorbed in 4 hours at 26·6° C.			0·0016

Taking into account the composition of the filtered boiled water, the acids and bases may be combined as follows, the numbers being in grains per gallon:—

Ferric oxide, Fe_2O_3	0·0159 (*a*)
Calcium carbonate, $CaCO_3$	0·8078
Calcium nitrate, $Ca2NO_3$	0·0140
Calcium silicate, $CaOSiO_2$	2·0535
Calcium sulphate, $CaSO_4$	0·5199
Magnesium carbonate, $MgCO_3$ ..	1·4235
Magnesium sulphate, $MgSO_4$ ..	1·0900
Potassium carbonate, K_2CO_3 ..	0·1548
Sodium carbonate, Na_2CO_3	0·8726
Sodium chloride, NaCl	1·1550
Lithium chloride, LiCl	0·0831
	8·1901

Total solid constituents dried at 173° C., 8·295.

(*a*) Ferrous carbonate, 0·0232.

The analyses of the gases and the results of the bacteriological examination will form the subject of a further paper.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Continued from p. 286).

6. *Ammono Acids.*—The acid amides and imides derived from organic acids constitute a group of well known compounds, since practically every known carboxylic and sulphonic acid furnishes such a derivative. The amides and imides of the inorganic acids are not so well known, although in recent years several such compounds have been prepared and studied, among others especially the amides of sulphuric (Note 7) and nitric acids (Note 8) and the amides and imides of the acids of phosphorus (Stokes, *Am. Chem. Journ.*, pp. 1893—1898).

The members of the large group of acid amides and imides, in so far as they are soluble, give solutions in liquid ammonia which discharge the colour of alkaline solutions of phenolphthalein (Note 9), conduct the electric current, dissolve certain metals, and react with metallic amides, in a manner described in detail below, to give representatives of the class of ammono salts. The strength of these ammono acids, if it be assumed that their strength is indicated by the conductivity of their solutions in liquid ammonia and by the extent to which their salts resist the hydrolytic action of water, varies through quite as wide limits as do the ordinary oxygen acids. Acetamide and carbamide, at one extreme, for example, form solutions in liquid ammonia, which have scarcely more than an appreciable conductivity, and their potassium salts are completely hydrolysed in the presence of water. Toward the other extreme may be mentioned such ammono acids as phthalimide, nitrobenzenesulphonamide, nitrourethane, nitroguanidine, saccharin, &c., which dissolve in ammonia to form good conducting solutions (Franklin and Kraus, *Journ. Am. Chem Soc.*, 1905, xxvii., 191), and which form salts of the alkali metals which are more or less stable in the presence of water.

Further compounds which are to be included among the ammono acids are the amides and imides of the non-metallic elements. Just as the halogen derivatives of the strongly electronegative elements, such as arsenic, phosphorous, boron, silicon, are completely hydrolysed by the action of water, so we may expect the same compounds to undergo decomposition in contact with liquid ammonia, with the formation of products bearing relations to this solvent analogous to those which the hydrolytic products bear to water.

The following equations, giving the results of recent work, show that in fact such ammonolytic reactions take place :—

$3TeCl_4 + 16NH_3 = Te_3N_4 + 12NH_4Cl$ (Metzner, *Comptes Rendus*, 1897, cxxiv., 32).

$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH$ (Stock and Blix, *Ber.*, 1901, xxxiv., 3039).

$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl$ (Joannis, *Comptes Rendus*, 1903, cxxxv., 1106).

$PCl_3 + 5NH_3 = P(NH)NH_2 + 3NH_4Cl$ (Joannis, *Ibid.*, 1904, cxxxix., 364).

$AsCl_3 + 6NH_3 = As(NH_2)_3 + 3NH_4Cl$ (Hugot, *Ibid.*, 1904, cxxxix., 54).

$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl$ (Lengfeld, *Am. Chem. Journ.*, 1899, xxi., 531; Vigouroux and Hugot, *Comptes Rendus*, 1903, cxxxvi., 1670).

$SiS_2 + 4NH_3 = Si(NH)_2 + 2NH_4SH$ (Blix and Wirbelauer, *Ber.*, 1903, xxxvi., 4220).

$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 4NH_4Br$ (Blix, *Ber.*, 1903, xxxvi., 4219).

Tellurium nitride, Te_3N_4, is an acid nitride or an acid anammonide; boron imide, $B_2(NH)_3$, and boron amide, $B(NH_2)_3$, are ammonoboric acids; phosphorus imide amide, $NH=P{\cdot}NH_2$, is an ammonophosphorous acid; arsenious amide, $As(NH_2)_4$, is an ammonoarsenious acid; silicon amide, $Si(NH_2)_4$, and silicon imide, $Si(NH)_2$, are ammonosilicic acids, and sulphosilicourea, $SiS(NH_2)_2$, is a sulphoammonosilicic acid. As is pointed out below, at least some of these ammono acids may be expected to react with potassium amide to give the corresponding potassium ammono salts.

Representatives of still another class of ammono acids are the nitroanilines which are related to ammonia as the nitrophenols are related to water. Just as the acid properties and electrical conductivities of aqueous solutions of the nitrophenols increase rapidly with the number of nitro groups present in the benzene ring, so in the case of the nitroanilines it has been found that while ammonia solutions of aniline are practically non-conductors, dinitroaniline gives a solution which is a good conductor, and trinitroaniline forms solutions which approach the salts in the facility with which they convey the electric current (*Journ. Am. Chem. Soc.*, 1905, xxvii., 197). Metallic derivatives of trinitroaniline have not been prepared, although Franklin and Stafford have shown the probable existence of a potassium salt (*Am. Chem. Journ.*, 1902, xxviii., 102).

It is interesting in this connection to note other and similarly marked strengthening of the acid properties of certain acid amides by the introduction of negative groups. For example, liquid ammonia solutions of acetamide, urea, and urethane are very poor conductors, while cyanoacetamide, nitroguanidine, and especially nitrourethane (Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 205), form solutions which are excellent conductors. As was pointed out above, some of these ammono acids form salts which are stable in aqueous solutions, and in consequence have been prepared in considerable number in the past.

7. *Ammono Bases.*—The metallic amides, imides, and nitrides constitute a group of substances by no means so numerously represented among known compounds as is the case with the ammono acids. And among those that are known, as with the aquo bases it is the hydroxides of the alkali metals only which are soluble to any extent in water, so it is the amides of the alkali metals which are soluble in ammonia. Indeed, among the ammono bases potassium amide only (probably also rubidium and cæsium amides) is abundantly soluble.

Potassium amide has long been known, having been first prepared by Gay-Lussac and Thénard ("Recherches Physico-chimiques," 1811, i., 337) by heating metallic potassium in contact with gaseous ammonia. It is most conveniently prepared by the action of liquid ammonia on the metal in the presence of platinum black. The reaction between the metal and ammonia, which otherwise takes place very slowly (Joannis, *Comptes Rendus*, 1891, cxii., 502), is so greatly accelerated by the presence of the catalyser that any quantity of the amide may thus be very

* From *American Chemical Journal*, xlvii., No. 4.

easily made (Franklin, *Jour. Am. Chem. Soc.*, 1905, xxvii., 831). Potassium amide crystallises from cold concentrated liquid ammonia solutions in the form of beautiful colourless leaflets. Its solutions in liquid ammonia are good conductors of electricity (Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 290; Arrhenius's "Zubelband"). The basic properties of potassium amide are shown by its behaviour toward liquid ammonia solutions of phenolphthalein, and by its action on liquid ammonia solutions of oxygen acids, halogen acids, and ammono acids, and also by its action on metallic zinc. Its behaviour toward oxygen acids and halogen acids is represented by the equations $KNH_2 + NH_4NO_3 = KNO_3 + 2NH_3$, $KNH_2 + NH_4Cl = KCl + 2NH_3$. The action of potassium amide on the ammono acids and on metallic zinc is discussed in some detail further on in this paper.

Taking advantage of the solubility of potassium amide, the writer has been able to prepare a number of insoluble metallic derivatives of ammonia by bringing soluble metallic salts and potassium amide together in liquid ammonia solutions (*Journ. Am. Chem. Soc.*, 1905, xxvii., 833). The new substances are thus obtained as precipitates which may be purified and analysed and their identity thereby established. It has been found that potassium amide in ammonia solution reacts with silver nitrate to form silver amide, with lead nitrate or iodide to form lead imide, with mercuric bromide and iodide to form mercuric nitride, and with bismuth bromide and iodide to form bismuth nitride. These reactions are represented by the following equations:—

$$AgNO_3 + KNH_2 = AgNH_2 + KNO_3,$$
$$Pb(NO_3)_2 + 2KNH_2 = PbNH + 2KNO_3 + NH_3,$$
$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3,$$
$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3.$$

The close analogy between these reactions carried on in liquid ammonia solutions and the corresponding reactions in the water system will be clear from a comparison of the above equations with the following:—

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O,$$
$$Pb(NO_3)_2 + 2KOH = PbO.xH_2O + 2KNO_3 + (1-x)H_2O.$$
$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O,$$
$$2BiCl_3 + 6KOH = Bi_2O_3.xH_2O + 6KCl + (3-x)H_2O.$$

Just as in water solutions it is sometimes the hydroxide and at other times the oxide which is obtained, so in the case of the action of potassium amide on a silver salt in liquid ammonia it happens to be the amide which is formed; lead salts under similar treatment happen to give the imide, a deammonation product of the amide; while mercury and bismuth salts give neither the amide nor imide but in their stead the final deammonation product, the nitride.

In addition to the four ammono bases prepared as described above, Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 656) has shown that potassium amide acts upon cupric nitrate in solution in liquid ammonia to form cuprous nitride in accordance with the equation $3Cu(NO_3)_2 + 6KNH_2 = Cu_3N + 6KNO_3 + N + 4NH_3$, and it has been recently shown in this laboratory that a nitride of thallium is formed after the manner represented by the equation (experimental results not yet published) $3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$.

The new ammono bases thus obtained are insoluble in liquid ammonia, but dissolve readily in ammonia solutions of appropriate ammonium salts. Four of them—silver amide, lead imide, cuprous nitride, and thallium nitride—are amphoteric in character, for in addition to being soluble in ammonium salts, that is, in acids, they are also soluble in solutions of potassium amide. When dry, they all explode with more or less violence when heated or subjected to shock. Silver amide especially is so sensitive that it was only by exercising the greatest care that the isolation and analysis of the substance were accomplished. With the exception of mercuric nitride they are completely hydrolysed by the action of water with the evolution of ammonia and the formation of aquo bases. This exceptional behaviour of mercuric nitride is significant, as will be discussed in detail in a subsequent paper.

Soluble salts of a number of other metals, including calcium, barium, aluminium, ferrous and ferric iron, cadmium, magnesium, platinum, and nickel, have been found to give precipitates when treated in liquid ammonia solutions with potassium amide. It therefore appears certain that by this method a very considerable number of new metallic amides, imides, and nitrides may be prepared.

Before leaving the subject of the ammono bases it may be worth while to state that attempts have been made to prepare amides of the formulæ $(CH_3)_4N{\cdot}NH_2$, $(CH_3)_3S{\cdot}NH_2$, and $(C_6H_5)_2I.NH_2$ by the action of potassium amide on tetramethylammonium chloride, trimethylsulphonium iodide, and diphenyliodonium iodide respectively, but as yet without success.

Other ammono bases which have been prepared and are found described in the literature are the amides of zinc, sodium, lithium, rubidium, cæsium, calcium, barium, and strontium, the imide of lithium, and a considerable number of metallic nitrides.

8. *Ammono Salts.*—The obvious parallelism between water and its derivatives, the acids, bases, and salts on the one hand, and ammonia with its family of derivatives, the metallic amides, the acid amides, and the ammono salts on the other, led the writer, collaborating with O. F. Stafford, to study in some detail the reactions between the acid and basic amides in solution in liquid ammonia (*Am. Chem. Journ.*, 1902, xxviii., 83). The result of these studies was to show that the acid amides, which discharge the red colour of an alkaline solution of phenolphthalein in liquid ammonia, react with soluble metallic amides, which give the characteristic red colour with the same indicator, to form metallic derivatives of the acid amides in a manner strictly analogous to the familiar formation of salts in aqueous solution by the interaction of the ordinary acids and bases. For example, acetamide and potassium amide react with each other in ammonia solutions to form monopotassium acetamide, a compound which must be called an ammonoacid salt—acid for the reason that it contains a hydrogen atom replaceable by metal—and dipotassium acetamide, a normal salt, in accordance with the equations—

$$CH_3CONH_2 + KNH_2 = CH_2CONHK + NH_3$$

and—

$$CH_3CONH_2 + 2KNH_2 = CH_3CONK_2 + 2NH_3,$$

which are seen to represent reactions which are analogous to the familiar action of acetic acid on potassium hydroxide in aqueous solution. In addition to these two compounds, Franklin and Stafford prepared the sodium salt of acetamide and the potassium salts of a considerable number of other acid amides (*loc. cit.*), among them urea and sulphamide, the ammonia analogues of carbonic and sulphuric acids respectively. Formulæ for some of these salts are given in the tables (*ante*). In general, any ammonia derivative containing a negative element or radical may be expected to react with any derivative of ammonia containing a positive element or radical to give a salt-like compound as represented by the equations $MNH_2 + AcNH_2 = MNHAc + NH_3$, $2MNH_2 + AcNH_2 = M_2NAc + 2NH_3$, &c.

Stafford and Franklin have also shown that ammono salts may be prepared by the reaction of ammonia solutions of ammono acids on certain metals. For example, acetamide in solution in liquid ammonia reacts upon metallic sodium in accordance with the equations—

$$CH_3CONH_2 + Na = CH_3CONHNa + H,$$
$$CH_3CONHNa + Na = CH_3CONNa_2 + H,$$

and upon metallic magnesium in a manner represented by the equation—

$$2CH_3CONH_2 + 4NH_3 + Mg = (CH_3COH)_2Mg.4NH_3 + 2NH,$$

which, as will be readily recognised, are equations which are strictly analogous to those representing the action

acetic acid on metallic sodium and magnesium respectively.

Magnesium benzenesulphonamide, $(C_6H_5SO_2NH)_2Mg$, and magnesium cyanoamide, CNNMg, were similarly prepared by the action of liquid ammonia solutions of the acid amides upon the metal.

Some of the ammono salts prepared by Franklin and Stafford are readily soluble in liquid ammonia, others are but slightly soluble or insoluble. Certain of them separate from solution with ammonia of crystallisation. They are hydrolysed completely in the presence of water. Their solutions in liquid ammonia are probably good conductors of electricity, although, unfortunately, this has been proved experimentally for but one representative of the class. Liquid ammonia solutions of mercuric succinimide are excellent conductors (*Journ. Am. Chem. Soc.*, 1905, xxvii., 196).

The soluble members of the class of ammono salts should also enter into metathetic reactions in liquid ammonia solutions, giving precipitates of insoluble ammono salts when the necessary metallic ion is added to their solutions. A solution of potassium acetamide, when added to a solution of silver iodide, for example, may be expected to give a precipitate of an ammonoacetate of silver. Unfortunately, however, such reactions have not yet been studied quantitatively.

A considerable number of metallic derivatives of the acid amides, that is to say, compounds belonging to the class of ammono salts, have been prepared in the past and are found described in the literature. It will be sufficient for our purpose to call attention to a few representative compounds.

Gal (*Bull. Soc. Chim.*, 1883, xxxix., 647) has prepared the zinc salts of acetamide, butyramide, benzamide, carbamide, and oxamide by the action of zinc amide, an ammono base, on the respective acid amides in ethereal solution, and Titherley (*Journ. Chem. Soc.*, 1897, lxxi., 461) has obtained the sodium derivatives of formamide, acetamide, propionamide, and benzamide by the continued action of hot benzene solutions of the acid amides on sodium amide (*Journ. Chem. Soc.*, 1897, lxxi., 461). The reactions whereby these products have been obtained are identical with those studied by Franklin and Stafford, excepting that the former were carried on in solvents other than liquid ammonia. Gal's and Titherley's compounds, like those prepared by Franklin and Stafford, are completely hydrolysed in the presence of water.

Salts of the stronger ammono acids, that is to say, the metallic derivatives of acid amides containing stronger electronegative groups, are capable of resisting the hydrolytic action of water to a greater or less extent, which accounts for the fact that a considerable number of such compounds—as, for example, the potassium and sodium salts of succinimide, phthalimide, saccharin, the nitrobenzenesulphonamides, and the nitroamines (Franchimont, *Rec. trav. chim.*, 1894, xiii., 308), nitrourea, nitrourethane, nitroguanidine (Thiele and Lachmann, *Liebig's Ann. Chim.*, 1895, cclxxxviii., 267), benzenesulphonnitroamide, &c. (Hinsberg, *Ber.*, 1892, xxv., 1093), have been prepared in the past from aqueous and alcoholic solutions.

The mercury and silver salts of the acid amides show a much greater resistance to the hydrolysing action of water than do the ammono salts of other metals. Mercuric ammono salts especially are unique in this respect. Mercuric acetamide, for example, is so very stable in the presence of water that even aqueous potassium hydroxide fails to effect its hydrolysis.

The metallic derivatives of the acid amides and imides have just been discussed at some length as members of the large class of ammono salts. The fact has not been forgotten, however, that the acid amides of oxygen acids are tautomeric substances (Hantzsch, *Ber.*, 1901, xxxiv., 3142); that is to say, they are compounds which behave sometimes in accordance with the one, and at other times in accordance with the other, of the two formulæ, $R—CONH_2$ and $R—C{<}^{NH}_{OH}$. The first formula represents the acid amide as an ammono acid, the second as a mixed aquo ammono acid. It may therefore well be that certain metallic derivatives of the acid amides, for example, acetamide mercury, are true ammono salts, whereas others, as potassium acetamide, are aquo salts. Certainly, however, in such a compound as dipotassium acetamide, one of the potassium atoms must be in combination with the nitrogen, and is therefore to that extent, at least, an ammono salt. Similarly, the metallic salts of other of the acid amides and imides mentioned above may be the tautomers of the true ammono salts. Potassium succinimide, for example, may be given the formula $CH_2CO{>}N$ instead of $CH_2CO{>}NK$; and potassium methylnitroamine, the formula $CH_3—N{:}NOOK$ instead of $CH_3—NK—NO_2$.

However all this may be, no such possibilities exist in connection with the metallic derivatives of the oxygen-free amides. In such compounds as silver cyanoamide, $CNNHAg$, potassium methylcyanoamide, $CNN(CH_3)K$, potassium succinimidine, $CH_2—C(NH){>}NK$, &c., there can of course be no question of the manner in which the metal is combined.

A considerable number of compounds belonging to the class of ammono salts are probably to be prepared by the action of potassium amide or of metallic potassium upon the non-metallic amides and imides, and perhaps even by the action of potassium amide upon the non-metallic nitrides. The only compound of this kind yet obtained is a potassium ammonotitanate, of the formula $N{\equiv}Ti—NHK$, which has been prepared in the chemical laboratory at Stanford University by Mr. T. B. Hine by the action of potassium amide in excess on titanium bromide (experimental results not yet published). The reaction is repre- by the equation—

$$TiBr_4 + 5KNH_2 = N{\equiv}Ti—NHK + 4KBr + 3NH_3.$$

Notes.

7. Traube, *Ber.*, 1892, xxv., 2472; 1893, xxvi., 610; Hantzsch and Holl, *Ibid.*, 1901, xxxiv., 3435; Ruff, *Ibid.*, 1903, xxxvi., 2900; Franklin and Stafford, *Am. Chem. Journ.*, 1902, xxviii., 95; Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 191; Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 300.

8. Thiele and Lachmann, *Liebig's Ann. Chem.*, 1895, cclxxxviii., 267; Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 191.

9. A large excess of such an acid as acetamide is required to discharge the red colour of a solution of phenolphthalein which has been rendered alkaline by potassium amide, obviously for the reason that acetamide is a very weak acid whose salts in solution in liquid ammonia are highly ammonolysed.

(To be continued).

Carbon Nitrides.—H. Pauly and Ernst Waltzinger.—When the tetraiodide of imidazol is heated it gives up three atoms of iodine at 180°, and the fourth at 420°, the final product being the substance C_3N_2. C_3N_2 like paracyanogen gives dicyanogen at 800—900°, $C_3N_2 = (CN)_2 + C$. The product obtained at 180° is C_3N_2I, and resembles amorphous carbon. When α- or μ-methyl tri-iodoimidazol and tetraiodopyrrol are heated the products are $C_3N_2.CH_3$ and C_4NH respectively. They both give cyanogen when heated. When heated with soda lime they give up all their nitrogen as ammonia, and they readily dissolve in fused alkalis; ammonia is slowly given off, and CO_2 and HCN appear in the melt. These compounds seem to belong to a new class of substances, to which paracyanogen also belongs.—*Berichte*, xlvi., No. 13.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Light of the Marine Abysses.

The depths of the oceans and seas have for a long time excited the curiosity of learned men. An unknown fauna has been revealed by the soundings effected during the cruisings of the Prince of Monaco. One question, however, remained obscure: that of the penetration or light into the marine abysses. Was it complete obscurity or slight luminescence? M. Klaus Grein has just made known in the *Annales of the Oceanograph Institute* the result of the researches he undertook for the last two years in the transparent waters of the island of Capri. The absorption of light by sea-water is progressive. From a depth of 5 metres the bluish violet rays form more than the half of the totality of light. M. Grein and his collaborator, M. Ewald, have then searched, with the help of sensitive films in the bluish violet region of the spectrum, what is the quantity of light that penetrates into the depth of the water. He took as a luminous unity the quantity of light existing at a degth of 3 metres. At 20 metres the light decreases by half, by two-thirds at a depth of 30 metres, and five-tenths at 40 metres from the surface. At a depth of 75 metres only a fiftieth part of the light existing at 3 metres depth passes, and only the three hundred and thirtieth part at a 100 metres from the level of the sea. Other experiments have been made at Monaco by this physicist. He has remarked that at a depth of 50 metres only a two-millionth part is to be found of the red light existing at 1 metre; orange resists longer. But it is in the green part of the spectrum that the luminous intensity is the slowest to diminish. The blue-green and the blue-violet penetrate even to the deepest depths. At 1000 metres there are ten times more blue-violet than blue-green; at 1300 metres and more these rays still make an impression on the plate. The light as it penetrates further and further through water diminishes in intensity. It descends beneath the threshold of human vision, beneath that of the assimilation of plants, but it is never extinguished.

The Erosion of the Sea Coasts.

In the war that the sea is daily waging against the coasts the land is often vanquished. The sea often, indeed, advances far inland, but there are also certain points where it is known to recede before the new land that emerges from the waves. The modifications of the southern coast of Brittany between Peumarch and the river Loire have just been studied from this point of view by M. La Porte, hydrographic engineer of the navy, who has compared the surveys of 1820 executed by Messrs. Beautemps and Beauchamp with the quite recent surveys effected from 1901 to 1911 by the hydrographic ordnance service. The conclusion of M. La Porte's paper, which has been presented before the Academy of Sciences by M. Hatt, is that the coast is receding towards the west of an axis passing by Quiberon, and is rising in the east. In the Morbihan district, on the contrary, a remarkable stability of the coast-line is to be observed. The maximum displacement seems to be about 12 centimetres in a century. Thus, in a region situated to the west of Quiberon the sea has taken on an average about 40 metres from the coast, and in some places as much as 60 metres in a hundred years. Towards the Loire, on the contrary, it is the land that is enroachiug on the sea.

Radio-culture.

M. Stoklasa, of Prague, is continuing his researches on radio-culture. He has been able, by submitting different cultures to radio-active action, either natural or artificial, to considerably increase the weights of the crops, compared with those produced by ordinary culture, it is essentially useful to rigorously dose the radio-active energy put into play, for same influence, after a certain maximum is reached, becomes unfavourable, and may even bring about the death of the plant. These results, communicated by Prof. Maquenne, are of the greatest interest from a biological and also from an agronomical point of view, for it is quite possible that big agricultural enterprises may, in the long run, benefit by these early indications. As a matter of fact, it suffices, in order to put into practice M. Stocklasa's experiments, to water the ground with water naturally radio-active, which may sometimes be procured without difficulty, or else water charged with emanations of radium may be employed. It may, perhaps, be that in the activity of the soil or the sub-soil is to be found an explanarion of the particular fertility of certain regions, which up till now has not been thoroughly understood, either by the composition of the soil or by the climatic conditions of the spot.

SIR JOHN CASS TECHNICAL INSTITUTE.

The Annual Prize Distribution was held on December 10th, when the prizes were distributed by Sir Thomas H. Elliott, K.C.B., Deputy Master and Comptroller of the Royal Mint. The Chair was taken by Sir Owen Roberts, M.A., D.C.L., Chairman of the Governing Body of the Institute.

Sir Thomas Elliott, in addressing the students, spoke of the desirability of keeping in view the aim of the instruction provided at the Institute, the object of its work, and the extent to which this object was being accomplished. He was himself disposed to say that the primary purpose for which the Institute exists is to assist students to do justice to themselves and to those who may be or become dependent upon them, to enable them to perform services which the community requires and for which the community is prepared to pay and to pay well, to increase their earning powers, and so to help them to secure a better livelihood for themselves than would otherwise be theirs. At the same time he, of course, fully realised that men could not live by bread alone, but that the building up of the bodily health, the broadening of the mental powers, and the development of the moral character were also essential to individual happiness and national prosperity. The achievement of these things is, however, much more difficult unless a man has continuous, regular, and remunerative employment, and it is to assist in making sure of such employment that the work of the Institute is mainly directed. Sir Thomas Elliott also counselled the students not to be afraid of selecting a manual occupation, and in connection with it to endeavour to learn all the facts connected with the material used, the machinery employed, and the scientific principles upon which the work is based. With such knowledge, students should be in a position to take advantage of the two or three chances which come to most men in the course of their lifetime of rising out of the rank and file and of getting as it were their commission with all its attendant privileges and responsibilites. In this connection also he advised the students to be a little adventurous and ambltious and not to play overmuch for safety.

The Rev. J. F. Marr, M.A., Chairman of the Institute Committee, gave a summary account of the work of the Institute during the past session, in which he referred especially to the increasing number of students, the research work that had been carried on in the Institute both by students and by members of the staff, and the several developments in the courses of instruction provided; in this latter connection details were given of the work on Colloids, on the Theory and Applications of Mathematical Statistics, on the Fermentation Industries, on Mine Sampling and Valuing, on Metals used in the Motor Car Industry, and on the Casting of Metals, all subjects which had received the special attention of the Governing Body during the past session.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows :—

"*On a Method of Studying Transpiration.*" By Sir FRANCIS DARWIN, F.R.S.

In order to study the effect of external conditions on the evaporation of water from leaves, it is necessary to exclude the action of the stomata from the problem, because the opening and closing of these apertures practically increase and diminish the evaporating surface. This is evident, since the leaf is made up of transplanting cells and intercellular air spaces, and it is the connection of these spaces with the outer air that is controlled by the stomata.

The method I employ is to close the stomata by coating the surface of the leaf with vaseline or some other grease, and then to place the intercellular spaces in connection with the outer air by cutting the leaf into strips. It is found by experience that such leaves transpire at rates comparable to those observed in natural leaves, and that they appear to behave normally in relation to external influences. In the present paper the effect of the relative humidity of the air is considered.

The diagrams constructed from the experiments show in a general way the obvious fact that transpiration falls off as the air becomes more charged with moisture. The diagrams also illustrate the well-known fact that transpiration continues in saturated air in consequence of the temperature of the leaf being above that of the air. This is well known to be due to the respiration of the leaf, and is of interest that the diagrams give a means of calculating of leaf temperature.

Finally, my results point to an improved but rough method of expressing the relation between transpiration and the psychometric condition of the air. This makes it possible, in studying the effect of other conditions on transpiration, *e.g.*, the action of light, to introduce a correction for psychrometric differences.

"*The Effect of Light on the Transpiration of Leaves.*" By Sir FRANCIS DARWIN, F.R.S.

The method employed is that described in my paper "On a Method of Studying Transpiration." The stomata are closed by a coating of vaseline, and the intercellular spaces are placed in communication with the outer air by means of slits or other incisions in the leaf. In this way we avoid the difficulty inherent in the problem of normal transpiration, viz., that this process is regulated by apertures (the stomata) which are constantly varying in size.

The object of the research was to get a general idea of the differences in transpiration produced by alternate periods of diffused light and darkness. The experiments were made on the laurel (*Prunus laurocerasus*) and the ivy (*Hedera helix*), either by weighing or with the potometer.

The results proved variable, and only by taking an average of a considerable number of experiments were figures of any sort of value obtained. For *Prunus* the average transpiration-rates in light and darkness are as 132 : 100 ; for ivy the figures are 136 : 100.

"*On Dimensions of Chromosomes considered in Relation to Phylogeny.*" By Prof. J. B. FARMER, F.R.S., and L. DIGBY.

"*The Process of Calcification in Enamel and Dentine.*" By J. H. MUMMERY.

Although much has been written on the calcification of teeth, the actual mode of deposition of the lime salts has been very little investigated. The author shows that both in dentine and enamel the lime salts are deposited in the globular form, despite the chemical composition of the finished tissues.

This fact is probably due to preponderance of carbonates in young tissues, as lime salts are not deposited in globular form in colloid substances when phosphates are in excess.

In drawing attention to the large part played by physical processes in calcification, the dialysis of lime salts and their deposition as calcospherites is shown in osmotic growths in chemical solutions. A repetition of some experiments of Rainey and Harting on the production of calcospherites shows that two typical forms are found in gum and in albumen, the radial and the concentric. The radial form is especially noticeable in the calcifying shell of crustacea.

It is seen that the typical form in dentine is the concentric, this structure being visible in the deeper parts of the forming dentine, the calcospherites when first deposited being clear and apparently structureless.

The lamellæ of dentine are seen to be due to extension of the elements of the calcospherites. In enamel the typical form is "radial," these calcospherites being clear and generally of an oval form in human enamel, but where undergoing disintegration they show radial splitting.

They are best seen in the enamel of marsupials where there is an abundant organic basis, and the spherites which are spherical in these animals are found lying between the laminæ, into which the enamel breaks up in teazed preparations, in all stages of disintegration.

In man they are found nearer the forming surface and immediately beneath the enamel organ, many having a diameter four times that of the enamel prism. It is shown that the sheath of Neumann has an independent existence apart from the fibril, and a study of the shell of Brachiopoda shows a similar acid-resisting membrane surrounding the tubes containing the protoplasmic prolongations from the mantle.

"*The Optimum Temperature of Salicin Hydrolysis by Enzyme Action is Independent of the Concentrations of Substrate and Enzyme.*" By ARTHUR COMPTON.

An experimental inquiry to ascertain if variations in the concentrations of an enzyme and its substrate have any effect on the optimum temperature of the enzyme. The enzyme action investigated has been the hydrolysis of salicin by an extract of sweet almonds. It is found for an action of 15 hours' duration that the optimum temperature of the reaction remains constant at 34° C. This temperature continues to be the most favourable in experiments where the concentrations of enzyme and substrate have been varied, either separately or together. The optimum temperature of the enzyme in question is, therefore, independent alike of the concentration of the substrate and of the concentration of the enzyme.

"*The Ratio between Spindle Lengths in the Spermatocyte Metaphases of Helix Pomatia.*" By C. F. U. MEEK.

"*Egyptian Blue.*" By A. P. LAURIE, D.Sc., W. F. P. MCLINTOCK, and F. D. MILES.

The purpose of the research is to decide the exact conditions under which the blue, manufactured and used in Egypt from the 4th dynasty to classical times, is produced, and to clear up the doubts as to its nature and constitution.

The results of the investigation are to confirm the conclusion come to by Fouqué that the blue is a double silicate consisting principally of calcium and copper, but in which these metals can be partially replaced by alkalis.

When soda, lime, and copper carbonate are heated with an excess of sand, a green glass is formed round the quartz particles at about 800° C. At about 840° the double silicate begins to crystallise out of this magma, again completely dissolving to form a green glass at 890°. The discovery of this compound by the Egyptians is doubtless due to their practice of glazing small articles carved out of sandstone with a green copper glaze.

CHEMICAL SOCIETY.

THE following communications have been received during the vacation :—

261. "*The Mechanism of the Benzoin Synthesis.*" (Preliminary Note). By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

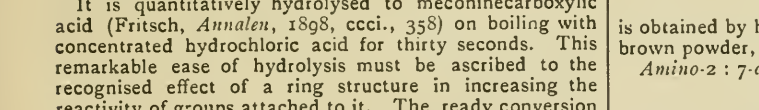
The investigation originated with the observation that cotarnine condenses with many aromatic aldehydes to form bases which are probably benzoylhydrocotarnines. With the idea of improving the yield and guided by Lapworth's well-known explanation of the benzoin synthesis, the authors attempted to prepare benzoyl hydrocotarnine (or its cyanohydrin) by the condensation of cotarnine with mandelonitrile in alcoholic solution; the products were, however, cyanohydrocotarnine and benzaldehyde. Cyanohydrocotarnine was also obtained when benzoylmandelonitrile (Francis and Dale, *Trans.*, 1909, xcv., 1404) was mixed with an equimolecular amount of cotarnine in alcoholic solution. In this case the expected benzaldehyde and benzoic acid were produced in traces only; the main products were benzoylbenzoin (m. p. 125°) and ethyl benzoate, as well as a small proportion of benzyl benzoate. A similar result was achieved when the cotarnine was replaced by sodium acetate, potassium carbonate, or sodium ethoxide. With the latter the reaction is complete, and may be expressed by the equation :—

$$2BzO\cdot CHPh\cdot CN + 2NaOEt = BzO\cdot CHPh\cdot COPh + Ph\cdot CO_2Et + EtOH + 2NaCN.$$

α-Cyanomeconine, $C_6H_2(OMe)_2<^{CH(CN)}_{CO-\!\!-\!\!-}>O$.

Opianic acid (1 mol.) and potassium cyanide (1 mol.) react in aqueous solution with the production of the potassium salt of the cyanohydrin of opianic acid. The acid is a syrup readily soluble in water, and passes very slowly into the corresponding lactone, α-cyanomeconine; the loss of water occurs rapidly on boiling its solution in dilute hydrochloric acid. The substance crystallises from methyl alcohol in prismatic needles, melting at 100—101°), and is sparingly soluble in alcohol or ether.

It is quantitatively hydrolysed to meconinecarboxylic acid (Fritsch, *Annalen*, 1898, ccci., 358) on boiling with concentrated hydrochloric acid for thirty seconds. This remarkable ease of hydrolysis must be ascribed to the recognised effect of a ring structure in increasing the reactivity of groups attached to it. The ready conversion of α-cyanomeconine to tetramethoxydiphthalyl by alkaline agents is analogous to the above production of benzoylbenzoin, and is best effected by potassium cyanide or cotarnine. The meconine hydrogen atom may be partly substituted by potassium (or cotarninium), and this intermediate substance may then condense either with itself :—



or with a molecule of cyanomeconine, in which case a further substitution of hydrogen by potassium, followed by loss of potassium cyanide, must occur before tetramethoxydiphthalyl is reached. A similar series of reactions may explain the more complicated production of benzoylbenzoin, although there are alternative methods of expressing the elimination of ethyl benzoate. The authors consider that the formation of benzoin itself is concerned entirely with the aldehydecyanohydrin in its double function as reactive cyanide analogous to ethyl iodide, and as a phenylacetonitrile with a hydrogen atom displaceable by alkali metals.

The action of potassium cyanide on mandelonitrile in boiling alcohol yields an oil which is probably benzoincyanohydrin; on treatment with sodium hydroxide in the cold, benzoin is produced. Many attempts to prepare mixed benzoins by different methods have been unsuccessful.

Incidentally, the authors have investigated the hydrolysis of acyl cyanohydrins, and find that these compounds are very well adapted for the preparation of mandelic acids. Benzoylmandelonitrile gives a good yield of benzoic and mandelic acids on prolonged boiling with concentrated hydrochloric acid, whilst on solution in sulphuric acid and subsequent dilution with water, benzoylmandelamide, $BzO\cdot CHPh\cdot CO\cdot NH_2$, is obtained. The latter crystallises from ethyl alcohol in feathery needles melting at 160—161°. Saturation of a solution of benzoylmandelonitrile (1 mol.) and ethyl alcohol (2 mols.) in dry ether with hydrogen chloride at 0°, and decomposition after twelve hours with alcohol and water, produces *ethyl benzoylmandelate*, $BzO\cdot CHPh\cdot CO_2Et$, a viscid oil boiling at 227°/20 mm., together with a relatively small quantity of benzoylmandelamide.

Benzoyl-o-nitromandelonitrile, obtained in excellent yield from *o*-nitrobenzaldehyde, aqueous potassium cyanide, and benzoyl chloride, crystallises from alcohol in pale yellow needles melting at 89°, and yields on hydrolysis with concentrated hydrochloric acid, benzoic and *o*-nitromandelic acids.

262. "*Some Derivatives of Phenanthraquinone.*" (Preliminary Note). By KSHITISH CHANDRA MUKERJEE and EDWIN ROY WATSON.

An investigation has been undertaken with the object of preparing derivatives with valuable dyeing properties from phenanthraquinone. Up to the present the following compounds have been obtained :—

Nitro-2 : 7-diacetoxyphenanthraquinone,—

$$C_{14}H_5O_2(OAc)_2\cdot NO_2,$$

Prepared by dissolving 2 : 7-diacetoxyphenanthraquinone in cold nitric acid (D 1·39) and plunging the containing vessel for one and a-half minutes into boiling water, crystallises from a mixture of acetic acid and acetone in yellowish brown rhombic prisms, which do not melt below 290°.

Nitro-2 : 7-dihydroxyphenanthraquinone,—

$$C_{14}H_5O_2(OH)_2\cdot NO_2,$$

is obtained by hydrolysing the above acetyl derivative as a brown powder, which does not melt below 290°.

Amino-2 : 7-dihydroxyphenanthraquinone,—

$$C_{14}H_5O_2(OH)_2\cdot NH_2,$$

prepared by reducing the nitrodiacetoxyphenanthraquinone with tin and hydrochloric acid and treating the product with warm ferric chloride solution, consists of deep brown small rectangular plates, is insoluble in all ordinary organic solvents, dissolves in alkali hydroxide with a brown colour, and does not melt below 290°. Its *triacetyl* derivative, $C_{14}H_5O_2(OAc)_2\cdot NHAc$, does not melt below 295°.

2 : 7 : ?-Trihydroxyphenanthraquinone, $C_{14}H_5O_2(OH)_3$. —The aminohydroxy-compound is diazotised in ice-cold 10 per cent sulphuric acid, and the filtered diazo-solution on boiling-precipitates the trihydroxyphenanthraquinone as a reddish brown substance, which does not melt below 290°, can be dissolved in pyridine and precipitated by alcohol, and dissolves in alkali with a brown colour. Its *triacetyl* derivative, $C_{14}H_5O_2(OAc)_3$, deposited as a reddish brown microcrystalline powder from glacial acetic acid, melts at about 280°.

2 : 7-Diacetylaminophenanthraquinone, $C_{14}H_6O_2(NHAc)_2$, is prepared by heating 2 : 7-diaminophenanthraquinone with acetic anhydride and fused sodium acetate at 160° for one hour in a sealed tube. It is a chocolate-brown coloured substance, readily soluble in acetic acid, sparingly so in alcohol, and does not melt below 295°.

Phenanthraquinone-2 : 7-bisazophenol,—

$$C_{14}H_6O_2(N_2\cdot C_6H_4\cdot OH)_2,$$

prepared by diazotising 2 : 7-diaminophenanthraquinone in 5 per cent sulphuric acid and coupling with phenol, crystallises from a mixture of alcohol and nitrobenzene in

brown lenticular crystals, which do not melt below 295°, and dissolve in alkali with a brown colour. The *diacetyl* derivative, $C_{14}H_6O_2(N_2{\cdot}C_6H_4{\cdot}OAc)_2$, crystallises from acetic acid in brick-red rhombic prisms, melting at 274°.

263. "*Some Derivatives of* 2 : 3 : 4 : 2′-*Tetrahydroxybenzophenone.*" (Preliminary Note). By NARENDRA NATH SEN GUPTA and EDWIN ROY WATSON.

This investigation has been undertaken with the object of preparing dyes of deep colour by replacing the ketonic group of the polyhydroxybenzophenones by the arrangement CR(OH). Up to the present the following derivatives of 2 : 3 : 4 : 2′-tetrahydroxybenzophenone have been prepared.

2 : 3 : 4 : 2′-*Tetrahydroxy*-4″-*dimethylaminotriphenylcarbinol anhydrohydrochloride*,—

$$C_6H_2(OH)_3{\cdot}C(C_6H_4{\cdot}OH){:}C_6H_4{:}N(CH_3)_2Cl\ (?),$$

prepared by the action of a mixture of dimethylaniline and phosphoryl ohloride on the tetrahydroxybenzophenone, is a crimson amorphous substance, melting at 184—185°, and decomposing at 200°, which dyes crimson shades on wool mordanted either with chromium or tin.

2 : 2′-*Dihydroxy*-3 : 4-*dimethoxybenzophenone*,—

$$HO{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}C_6H_4{\cdot}OH,$$

obtained by the interaction of *o*-methoxybenzoyl chloride and pyrogallol trimethyl ether in the presence of anhydrous aluminium chloride, crystallises from alcohol in yellow needle-shaped crystals, melting at 127°.

2 : 3 : 4 : 2′-*Tetramethoxybenzophenone*,

$$C_6H_2(OMe)_3{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

obtained by the action of methyl sulphate and potassium hydroxide on tetrahydroxybenzophenone or on 2 : 2′-dihydroxy 3 : 4-dimethoxybenzophenone, crystallises from dilute alcohol in colourless prisms, melting at 83°. Its *phenylhydrazone*, $C_6H_2(OMe)_3{\cdot}C(:N{\cdot}NHPh){\cdot}C_6H_4{\cdot}OMe$, crystallises from alcohol and melts at 153°. Its *oxime*, $C_6H_2(OMe)_3{\cdot}C(:NOH){\cdot}C_6H_4{\cdot}OMe$, crystallises from alcohol and melts at 166°.

The *pinacone*,—

$$C_6H_2(OMe)_3{\cdot}C(C_6H_4{\cdot}OMe)(OH){\cdot}{\cdot}C(C_6H_4{\cdot}OMe)(OH){\cdot}C_6H_2(OMe)_3,$$

obtained by the action of zinc dust and acetic acid on the tetramethoxybenzophenone, is purified by crystallising in succession from glacial acetic acid and alcohol, and forms colourless needle-shaped crystals, melting at 185 – 186°.

264. "*The Constitution of Phenolphthalein and its Alkali Salts.*" By MORRIS FORT and FRANK LESLIE BARRETT.

Green and Perkin (*Trans.*, 1904, lxxxv., 398) have described a method of titrating a cooled colourless solution of phenolphthalein in a known excess of potassium hydroxide with acetic acid. Using 0·5 grm. of phenolphthalein, they found 17·6 per cent of potassium hydroxide to remain unestimated by the acid, that is, the amount calculated for $C_{20}H_{15}O_5K$. The titrated solution was clear and colourless, becoming deep red and alkaline to litmus on heating, whilst a precipitate of phenolphthalein also separated out, and on again cooling these features persisted. It does not appear from the account of this work that the possible reaction between phenolphthalein and potassium acetate had been taken into account, whereas it is now found that a colourless mixture of these two substances in solution becomes red and alkaline to litmus on heating, remaining so on keeping until cold. The reaction is by no means unique, and belongs to the class of "neutral salt reactions" due to the operation of mass law (Fort, *Journ. Soc. Dyers*, 1912, xxviii., 314; 1913, xxix., 80, 120, 269; CHEM. NEWS, 1913, cviii., 1). The mere colour changes occurring on heating after titration as described have since been instanced in support of the quinonoid theory of colour (Green, *Journ. Soc. Chem. Ind.*, 1908, xxvii., 4), but now lend no support apart from the quantitative results, which appear liable to a considerable working error, being calculated from 0·65 cc., where 0·1 cc. = 3·7 per cent KOH.

Green and Perkin's experiment was therefore repeated, using also larger amounts of phenolphthalein up to 3 grms., and a series of results was obtained varying within the limits of error assigned above, for example, 16·65, 18·14, 16·10, &c. The average of ten successive experiments gave 17·54 per cent of potassium hydroxide ($C_{20}H_{15}O_5K$ requires 17·6 per cent KOH). (*a*) The amount of potassium combined with phenolphthalein as a colourless salt was also estimated directly with acetic acid, after heating and re-cooling with ice, and found to agree with the above indirect estimation. (*b*) At the same time, to decide as to the condition of phenolphthalein and the equilibrium obtaining in the red alkaline solution, the colourless solution of the monopotassium salt was closely imitated with a red solution containing fresh phenolphthalein, potassium hydroxide, and potassium acetate, and these intensely red and colourless liquids were heated side by side until of a similar intense red, behaving quite similarly on cooling with ice and titrating with acetic acid. There can therefore be little doubt as to the isomeric change taking place from the less stable colourless monopotassium salt of phenolphthalein, to the coloured quinonoid salt. (*c*) Neutral salt reactions are greatly retarded by lowering of temperature as in the titrations in (*a*) and (*b*); however, in order to determine the highest possible error from this cause, a blank experiment with phenolphthalein and potassium acetate was performed alongside (*a*) and (*b*), showing that the quantitative results are liable to be affected by the neutral salt reaction to only a small extent.

The experiments were made in duplicate, comparative throughout. The potassium hydroxide solution contained 177·184 grms. of the alkali per litre, and 25 cc. of the acetic acid were equivalent to 20·6 cc. of potassium hydroxide solution.

(*a*) One grm. of phenolphthalein and 20 cc. of potassium hydroxide solution were taken; after preparation of the colourless salt it was heated in the water-bath one hour under an air condenser, cooled with ice, and titrated to a permanent pale pink colour requiring 1·20 cc. of acetic acid = 17·5 per cent KOH. The faint pink at the end-point can be removed with a considerable excess of acetic acid, and is ascribed to the presence of potassium acetate, $C_{20}H_{15}O_5K + C_2H_4O_2 \rightleftharpoons C_2H_3O_2K + C_{20}H_{16}O_5$.

(*b*) One grm. of phenolphthalein, 9·95 cc. of potassium hydroxide solution, and 6·1968 grms. of anhydrous potassium acetate were used; the volume was as in (*a*) after the preparatory titration. The solution was heated, cooled, and titrated as in (*a*) to a pale pink: 1·2 cc. of acetic acid were required = 17·5 per cent KOH. ($C_{20}H_{15}O_5K$ = 17·6 per cent KOH).

(*c*) One grm. of phenolphthalein and 6·1968 grms. of potassium acetate were used, the volume being as in (*a*) and (*b*), alongside which the solution was heated, cooled, and titrated to a pale pink: 0·12 cc. of acetic acid was required = 1·7 per cent KOH. The intense red colour given on heating is largely retained at the ordinary temperature, but much reduced at 0°. The figure obtained from a duplicate experiment titrated at the boiling-point after an hour's heating in the water-bath was 0·29 cc. of acetic acid = 4·23 per cent KOH.

These results support the main conclusions drawn by Green and Perkin, and are in agreement with the quinonoid formulæ adopted by them for coloured phenolphthalein salts.

265. "*Complex Metal Ammonias.* cis-*Sulphonyldiacetatodiethylenediaminecobaltic Hydrogen Sulphonyldiacetate.*" (Preliminary Note). By THOMAS SLATER PRICE and SIDNEY ALBERT BRAZIER.

In his investigations of the complex cobalt ammonias, Werner has prepared a number of salts of the type [A.Co en$_2$]X, where A is the radicle of a dibasic acid. So far the sulphito-, carbonato-, oxalato-, and malonato-radicles have been introduced into the complex, but Werner has not been able to obtain crystalline compounds

containing the next higher homologue to the malonato-radicle, namely, the succinato-radicle, or containing the radicles of malic and tartaric acids (*Annalen*, 1911, ccclxxxvi., 81). It occurred to the authors that the introduction of the sulphur atom into the chain of carbon atoms in the acid used might lead to interesting results in this connection, and Prof. Werner having kindly informed them that he did not contemplate working with such compounds, and would leave the field open to them, an investigation was commenced, using thiodiacetic acid, $S(CH_2{\cdot}CO_2H)_2$. Definitely crystalline compounds were obtained, but the results were complicated by the fact that during the preparation, partial reduction of the cobalt compound took place, and the authors have not yet been able to characterise the compounds formed. In order to avoid this complication, the thiodiacetic acid was replaced by sulphonyldiacetic acid, $SO_2(CH_2{\cdot}CO_2H)_2$, and the compound cis-*sulphonyldiacetatodiethylenediaminecobaltic hydrogen sulphonyldiacetate*,—

$$\left[O_2S<\begin{matrix}CH_2\cdot CO\cdot O\\ CH_2\cdot CO\cdot O\end{matrix}>Co\ en_2 \right] CO_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2H,$$

has been prepared.

The method of preparation was similar to that used by Werner for the corresponding malonato-compound (*loc. cit.*, p. 79). Four grms. of *cis*-carbonatodiethylenediaminecobaltic bromide were dissolved in 80 cc. of warm water, and, after cooling, 2·20 grms. of freshly prepared silver oxide were added to the solution. The mixture was well shaken for half-an-hour, and then filtered from the silver bromide into an aqueous solution of 5·63 grms. of sulphonyldiacetic acid, the proportions being 2 mols. of the acid to 1 mol. of the carbonato-base. The resulting solution, after evaporating to a small bulk on the water-bath, deposited crystals of the desired compound. One re-crystallation from water gave the pure salt, in dull rose-coloured microscopic crystals, which are readily soluble in hot, but somewhat sparingly soluble in cold water:—

0·2687 gave 0·0767 $CoSO_4$. Co = 10·86.
0·1797 gave 16·65 cc. N_2 (moist) at 19° and 749·3 mm. N = 10·45.
0·3045 gave 0·2618 $BaSO_4$. S = 11·81.
$C_{12}H_{25}O_{12}N_4S_2Co$ requires Co = 10·91; N = 10·37; S = 11·87 per cent.

The authors are extending the investigation to other sulphur compounds and complex metal ammonias.

Extra Meeting, October 23rd, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The Ladenburg Memorial Lecture was delivered by Prof. F. Stanley Kipping, D.Sc., F.R.S., and at the conclusion of the lecture a vote of thanks to Prof. Kipping was proposed by Prof. H. E. Armstrong, F.R.S., seconded by Prof. W. Jackson Pope, F.R.S., and acknowledged by the Lecturer.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, December 1st, 1913.

Dr. W. R. Hodgkinson in the Chair.

The following paper was read and discussed:—

"*Use of Antiseptics in Increasing the Growth of Crops in Soil.*" By E. J. Russell, D.Sc. and Walter Buddin, B.A.

The action of antiseptics on the soil is shown to be complex, but the most important for the present purpose is that the micro-organic population of the soil is very considerably simplified. The higher forms of life are killed when sufficient antiseptic is added, and the bacteria are greatly reduced in numbers.

If the antiseptic is volatile or easily removed from the soil a remarkable result is obtained shortly after it has gone. The bacterial numbers do not remain low, but they begin to rise and finally attain a level much exceeding that of the original soils. Simultaneously there is an increase in the rate of ammonia production in the soil; the evidence shows that this is the direct result of the increased numbers of bacteria. The increased ammonia production, however, does not set in if a large amount of ammonia and nitrate is already present in the soil.

This increased production of ammonia induces a larger crop growth than in the untreated soils; antiseptics, therefore, tend to have the same action as nitrogenous fertilisers and could be used to supplement them in practice.

The antiseptics also have more or less effect on disease organisms present in soils. These tend to be very prevalent under certain conditions of horticultural and agricultural practice, and their destruction is not effected by any of the methods ordinarily in use. Large growers are now using steam, and this is proving very effective; the treatment costs about 1s. a ton. Chemical treatment is at present less effective, but it appears capable of much improvement and of being finally carried out at less cost per ton. The requirements are that the antiseptics should be destructive to disease organisms, pests, and organisms detrimental to the ammonia producing bacteria, that it should be capable of being removed from the soil either by volatilisation, oxidation, or decomposition, and that it should be convenient in application, and should not be absorbed too readily by the soil, or proper distribution cannot take place. To be a commercial success it must be cheap and capable of being turned out to standard. Of the various compounds tried during the last three years, formaldehyde is the best, then comes pyridene, and then cresol, phenol, carbon disulphide, toluene, and others. None of these are as good as steam, but the subject is yet in its infancy, and there is no reason to doubt that suitable antiseptics will yet be found.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 3rd, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. John Joseph Eastick and J. F. Millar were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Rowland Holliday Ellis, "Lynwood," Thorpe Road, Selby, and Armand de Waele, "Rosemead," Sidney Road, Staines, Middlesex.

Certificates were read for the second time in favour of Messrs. Alan Milsom Bailey, Arthur Leslie Barton, Thomas Sidney Haines, and Arthur George Abraham Miller.

The following papers were read and discussed:—

"*Sulphuretted Hydrogen from Artificial Graphite.*" By W. H. Woodcock and Bertram Blount.

A sample of massive graphite manufactured by Dr. Acheson possessed the unusual property of evolving sulphuretted hydrogen when broken or rubbed. Investigation showed that this property was due not to occluded gas, but probably to the presence of a sulphide of the type of aluminium sulphide, which is decomposed on removal of the protective covering of graphite by contact with moist air.

"*Determination of Strychnine in the Presence of Quinine.*" By Charles Simmonds.

Strychnine can be accurately separated from quinine by precipitation as ferrocyanide in strongly acid solution, pro-

vided that certain conditions are observed as regards the proportions of acid and precipitant. The paper describes the requisite conditions, with experiments.

"*Rate of Liberation of Hydrocyanic Acid from Linseed.*" By S. H. COLLINS and H. BLAIR.

Linseed contains a cyanogenetic glucoside and an enzyme, which under certain conditions liberate hydrocyanic acid. The rate of liberation of hydrocyanic acid is modified by acids, alkalis, salts, poisons, digestive extracts, heat, moisture, other foods, mechanical condition, &c. Under practical conditions of feeding, dry linseed seems fairly safe, but linseed mash or soup needs to be prepared with care, under strict conditions. Insufficient heat, improper mixing, and lumpiness produce a linseed mash which is not safe for feeding calves.

"*Composition of Palm Kernel Oil.*" By GEORGE DAVIDSON ELSDON,

The author, in continuation of his work on alcoholysis (*Analyst*, 1913, xxxviii., 8) has examined palm kernel oil with the idea of finding some method of distinguishing it from cocoanut oil. No intrinsic differences have been found, and those which do exist are not sufficently great to form the basis of a method for differentiation of the oils. The composition of palm kernel oil is given.

"*Estimation of Sulphur in Rubber.*" By HENRY P. STEVENS.

Confirmation is given of the loss of sulphur during the oxidation of rubber products with nitric acid. The sulphur or sulphur product given off with the vapours may be retained by passing through solutions of caustic alkalis or nitric acid. For general purposes of analysis it is sufficient to carry out the decomposition in a large flask fitted with a Young's fractionating column, or in a large Kjeldahl flask provided with a 5 inch surface condenser fitting snugly into the neck. The figures for a large number of sulphur estimations are given in confirmation of the above.

"*The Insoluble Bromide Test for Drying Oils.*" By JOHN A. L. SUTCLIFFE.

The author has studied the influence of varying conditions upon the percentage of insoluble brominated glycerides obtained from linseed oil. A standard process is recommended, and the results obtained from linseed oils have been plotted as a curve against the iodine value. This curve is a straight line, of which the equation is:—Per cent of bromides = (0·63 iodine value) – 78.

NOTICES OF BOOKS.

Practical Science for Engineering Students. By H. STANLEY, B.Sc. (London and Bristol), F.I.C. London: Methuen and Co., Ltd. 1913.

ALTHOUGH intended primarily for the use of students in evening schools who have had some previous training in elementary science, it seems probable that this book might advantageously be adopted for rather different purposes. If supplemented by a certain amount of theoretical work it would give boys in secondary schools a thoroughly practical training in general physics, and also its clearness and conciseness should make it useful for revision work for candidates for examinations. The experiments described are such simple quantitative ones as can readily be performed without complicated or expensive apparatus. They are arranged in five sections on Heat, Mechanics, Magnetism and Electricity, Miscellaneous Experiments, and Materials respectively, but each section is independent of the others and the order in which they are taken is quite optional. The section on materials contains a few notes on some substances met with in engineering practice, *e.g.*, iron, cement, common acids, &c., and is intended rather to stimulate the student's intelligent curiosity than to satisfy it. Many problems and examples are given for calculation, and in all cases excellent schemes for the tabulation of results are provided.

Chemical German. By FRANCIS C. PHILLIPS. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1913.

IT is very necessary nowadays for the advanced student of chemistry to be able to read German easily, and a good many text-books on scientific German have appeared recently. Many of them, however, have included at least two or three branches of science, the editors overlooking the fact that what the student usually requires is a fairly thorough acquaintance with the nomenclature of one science only. This book on chemical German is intended for the student of chemistry, and the author has wisely presupposed in his readers a knowledge of the elements, both of the language and the science. Such special points as the nomenclature of compounds are explained in detail, and a set of exercises is provided for practice in reading. These are carefully graduated in difficulty, the first having been written specially for the book; the later ones are extracts from suitable text-books, and include some classical papers, such as that by Doebereiner on his triads and Kekulé's account of his vision of the benzene nucleus. Letters of famous chemists are also included and some short biographies. All branches of chemistry are treated, and the matter is always well chosen and interesting. Some notes are added, and occasionally, but not always, attention is called to statements in the text which later work has shown to be inaccurate. A vocabulary of words not likely to be found in an ordinary dictionary and a useful list of abbreviations are given; a few slips such as Recemkörper will want correcting in a new edition.

Vom Kohlenstoff. ("Carbon"). By HENRI LE CHATELIER. Translated by HERMANN BARSHALL. Halle (Saale): Wilhelm Knapp. 1913. (Mk. 18).

THIS book contains the introductory course of lectures on the principles of pure and applied chemistry delivered by M. Le Chatelier at the Sorbonne. The presentation of the subject differs fundamentally from the classical method, for the author believes that the best way to put the science before the student is to discuss, first of all, the quantitative laws of chemical mechanics, and afterwards to apply them to the special cases of a few reactions. Experimental facts are described only in so far as the consideration of them is necessary for the understanding of the laws, and carbon is selected as the most suitable element for providing illustrations. Hypotheses as to the constitution of matter are not treated at all, for the author considers that the beginner derives no benefit but rather positive harm from their study, since they induce him to accept debatable views as certain truths. There is undoubtedly still room for reform in methods of teaching chemistry, and this book seems to mark a distinct advance in the right direction.

Die Verwendung der seltenen Erden. ("The Use of the Rare Earths"). By Dr. C. RICHARD BÖHM. Leipzig: Veit and Co. 1913.

THE author of this book had originally intended to publish it in the form of a series of articles in "Die Chemische Industrie," but he found it impossible to condense all his material into a sufficiently small compass and accordingly decided to expand it into a book. The applications of the rare earths are divided into two classes:—Their employment in scientific work and in technical processes. Under the heading of the first class are included short accounts of the uses of the Röntgen rays and of radiology. The second section occupies the greater part of the book, and gives a complete critical review of the application of the

compounds of the rare earths in the incandescent gas-mantle and other industries. Moreover, the very numerous suggestions which have been made for other uses are noticed and their practicability discussed. These suggestions are grouped according to the property of the compound upon which the application is based, and the systematic arrangement of the text compensates to a certain extent but not entirely for a full index.

CORRESPONDENCE.

GALLIUM IN ALUMINIUM.

Quaternian Series.

To the Editor of the Chemical News.

Sir,—Mr. Ramage's letter in the Chemical News (vol. cviii., p. 280) gives information that I should have included in my paper referred to therein. Much of the work mentioned on gallium is given in Roscoe and Schorlemmer's "Treatise on Chemistry," in which Hartley and Ramage are quoted as follows:—"It occurs, for example, in a large number of iron ores, from which it passes into the iron prepared from them, so that Middlesbrough cast-iron contains as much as 1 part of gallium in 33,000 parts, and is the richest source of this element known." Its wide distribution in very minute quantities is also mentioned. Browning, in "Introduction to the Rarer Elements," cites instances of its wide distribution, and likewise mentions the work of these experimenters. It is interesting to note, nevertheless, that Boulanger and Bardet find that commercial aluminium contains 1 part of gallium in about 5900 parts, 1·7 kilogrms. of aluminium yielding 0·3895 grm. of gallium oxide.

I take this opportunity of adding a few notes. Referring to the Chemical News (cxviii., 247), if the sets of elements are arranged vertically in the order specified, it will be seen that those containing the halogens Cl, Br, and I, alternate between the sets containing Mg, Mn, Ru, and Te, and that the sum of the secondary differences ($a+b$, or $a+b+c$ in one case) is 28 in each series containing a halogen. The remaining series give corresponding values 3·82, 7·00, 17·49, and 45·27. The following table suggests a certain degree of regularity amongst all these values:—

1	$0\times3{\cdot}5$	= 0·0
1	$1\times3{\cdot}5$	= 3·5
1	$2\times3{\cdot}5$	= 7·0
3	$5\times3{\cdot}5$	= 17·5
3	$8\times3{\cdot}5$	= 28·0
5	$13\times3{\cdot}5$	= 45·5
5	$18\times3{\cdot}5$	

No series has, however, been given in which $a+b=0$. I now find that two or three series are possible which fulfil this apparent requirement, and which take up some outstanding elements analogous to those already appropriated. The members for these three extra series (which may be conveniently placed in another vertical column, so that they will stand opposite the others containing Cl, Br, and I) are:—C = 12, O = 16, F = 19, Na – 23; ?? = 68·88, Rh = 102·83, Ho = 163·30, Au = 197·25; Xe = 130·77, Nd = 144·28, Os = 190·50, Tl = 204·01. There may be Tl. and Tl[III]., differing slightly in atomic weight and chemically non-separable (see Soddy, Chem. News, cviii., 168), but it is hardly safe to assume, or even suggest as probable, that *all* the elements, especially those of low atomic weight, are thus *compounded* (using this word in its generic or general sense).

The parallelism in properties is fairly good. Oxygen has the same characteristic valency as beryllium and nickel, for example, and has a high positive magnetic susceptibility at very low temperatures (compared with such elements as manganese, chromium, palladium, titanium, and rhodium), thus in one respect linking itself up with the iron group. Rhodium resembles iron (see Mendeleeff's "Chemistry," ii., 403). Holmium (see gadolinium, previously considered) probably fits the gap beyond tellurium or iodine, when the method of classification is adopted as given in the Chemical News, xcix., 283. Osmium, ruthenium, and manganese are perhaps related to the halogens very much as gold, silver, and copper are related to the alkali metals, only in a kind of reverse sense.

In conclusion, I wish to thank Mr. Ramage for calling attention to the incomplete statement I made, and for the further data supplied.—I am, &c.,

F. H. Loring.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

Sir,—May I, as an outsider, be allowed to remark on the opinions expressed at the recent Conference of Professors of Chemistry *re* the Institute of Chemistry.

These mostly agreed that the present conditions of entrance are too narrow, being more accessible to the University chemist, to whom entrance is in many cases comparatively easy, than to the technical man, for whereas the latter is often a technical-academic chemist and therefore more qualified for the Institute of Chemistry, the former is usually only academically trained. That whereas the Institute wish to get all properly trained chemists under their regime, the present duplication of examinations and in some cases autocratic conditions of entrance are keeping away many who would do the Institute benefit. Also that research work should be a part of chemists' training, but only after he has acquired a good groundwork of scientific knowledge, such as the taking of a degree in chemistry.

As a suggestion for your readers' opinions and those concerned may I put forward the following:—

1. That the F.I.C. should bear the same relation to the A.I.C. as the D.Sc. does the B.Sc. And whereas the D.Sc. is the highest criterion of academic qualification, the F.I.C. should stand for technical skill together with a high scale of academic groundwork of scientific knowledge and some original research.

2. That a new qualification be considered, *i.e.*, a Membership of the Institute of Chemistry (M.I.C.).

3. That the gaining of any degree in chemistry, with or without honours by day or evening "internal" work should qualify for the Membership of the Institute of Chemistry (M.I.C.). In the case of evening work, only from Institutes under the strict supervision of the Institute of Chemistry.

4. That a M.I.C. should become qualified for the A.I.C. on the acceptance of a piece of original research work by the Institute. By research should be meant every branch of independent chemical investigation, either commercial or purely academic. Care would have to be taken to prevent this research developing into a species of post-graduate work, and research work under more technical experience-gaining conditions should be encouraged, since it was pointed out that even the honours and researched academic chemist still did not necessarily ensure the right professional qualifications.

5. That the somewhat mechanical step from the A.I.C. to the F.I.C. be changed and the F.I.C. be made more analogous to the qualification for Membership of the Institute of Civil Engineers. Thus an A.I.C. would be qualified for a Fellowship after, say, three or four years continuous practice in a responsible position in the chemical profession, and that very strict attention should be paid to the consideration of the manner in which the time has been spent.

It is certain that the entrance door to the Institute must be considerably widened if it is going to admit the true technical chemists. At present a man who for any reason does not wish to spend three continuous years at least at a recognised University is almost debarred from entrance—presumably for autocratic reasons of social distinction.

Such men who are gaining actual professional or technical experience in the daytime, or part of it, and are ambitious enough to work for their degree in the evening, are in the majority of cases probably far better qualified for entrance to the Institute, when they have taken their B.Sc., which naturally takes them longer, than those men who spend several continuous years gaining a University degree and take the A.I.C. soon after without any technical experience, and in three years automatically acquire the Fellowship. Amongst those in favour of extending the regulations so as to allow these men reasonable hope of admission, provided a qualifying general exam. be passed and that they have worked at a recognised Institute, are such authorities as Sir W. Ramsay, Prof. Kipping, and Dr. Keane, all of whom understand how the part-time and evening degree men are very badly hit by present regulations. The attitude which Sir W. Tilden takes up is typical of an attitude which the Institute must sever itself from if the majority of technical chemists are to be brought even to the state of desiring intimacy with the Institute of Chemistry. Sir W. Ramsay eaid that he considered that even laboratory boys who had taken their degree should be encouraged, and not kept under for the reason that they had not been sufficiently fortunate to have had the means for a University course, but Sir W. Tilden did not consider that the Institute should open its doors to even those laboratory boys who had made admirable chemists. He goes on to say:—"I do not say that you will not find extremely clever people amongst this class; the question is whether they will fairly represent professional chemistry if we help them to get into general practice; I think not, and it is on the ground of deficiency of general education I have in the past mainly felt an objection to admitting those students who come to the evening classes of many Institutions. Very many of these are most worthy, most industrious, very intelligent, but somehow I think that if we are going to build up a body comparable in social standing as well as professional rank with the great Institutions which have been referred to this afternoon, we must see that we do not admit too many of a class of persons who, whatever their other merits may be, are certainly not qualified to represent the Institute on public occasions and in the eyes of the world."

This is quite right in extreme theory, but does Sir W. Tilden think that all evening classes and part-timers are composed of laboratory boys, and that the admittance of the best of these "most worthy, most industrious, very intelligent" students necessitates them representing the Institute on public occasions and in the eyes of the world? We do not want the door opened wide so that all may flock in, but we do hope for a ray of light and hope, for at present there is almost none, and the way is so long and dreary as to not make it worth the ambition and perseverance required!—I am, &c.,

C. W. Wood.

King's College, University of London.

Literary Intelligence.—Messrs. J. and A. Churchill are about to publish the following new books and new editions:—"A Manual for Masons," by J. A. Van Der Kloes, Professor in the Science of Materials of Construction, Technical High School, Delft; revised by Alfred B. Searle. "Modern Steel Analysis," by J. A. Pickard, B.Sc., Honours London A.R.S.Sc., A.I.C., F.C.S., Carnegie Research Scholar of the Iron and Steel Institute. "The Story of Plant Life in the British Isles," by A. R. Horwood, Member of the British Botanical Society, Ecological, Conchological Societies, &c.; illustrated with seventy-three photographs. "Materia Medica, Pharmacy, Pharmacology, and Therapeutics," by W. Hale White, M.D., F.R.C.P.; 13th edition. "Elementary Practical Chemistry" (Part I.), by Frank Clowes, D.Sc.Lond., and J. Bernard Coleman, A.R.C.Sc.; Sixth Edition; with seventy-six illustrations. "The Medical Directory, 1914." "Who's Who in Science," 1914; with over 9000 Biographies.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 13, 1913.

Oxidation of Nitrogen in the Electric Discharge.—A. Koenig and E. Elöd.—The authors have investigated the oxidation of nitrogen during the electric discharge, using the experimental arrangement of Fischer and Hene, and their results have led them to the conclusion that there is no warrant for regarding the oxidation as due to the activation of the oxygen. Their experiments with continuous current arcs indicate that the chemical action of the gases mixed behind the arc is due to the fact that in consequence of the active motion of the gases in the region of discharge fresh quantities of gas are always being acted upon by the discharge.

Influence of Foreign Substances on the Activity of Catalysts.—C. Paal and Arthur Karl.—The authors have already shown that when palladium is precipitated on metallic Al, Fe, Cu, Zn, Ag, Sn, or Pb, it loses its power of rendering hydrogen active, and thus hydrogenating unsaturated compounds. The metals have the same effect in the form of oxides, hydroxides, and carbonates. This is specially noticeable in the case of basic lead carbonate, which completely prevents the catalytic action of palladium precipitated on it. On the other hand, the oxide of a metal such as magnesium, which does not influence the catalytic action of palladium, increases its activity owing to its greater surface.

Ammonium Peroxides.—J. D'Ans and O. Wedig.—When dry NH_3 is led into an absolute ether solution of pure H_2O_2, cooled to $-10°$, clear crystals separate after a short time. If more of the gas is passed in the crystals melt, and a thick oily liquid collects at the bottom of the vessel. The ethereal layer contains NH_3 and traces of H_2O_2. The crystals first formed are NH_4O_2H. They melt and decompose at about 14°. The oily layer solidifies to a crystalline mass at about $-40°$, and analysis shows that its composition corresponds to the formula $(NH_4)_2O_2$ (ammonium peroxide).

New Method of Preparation of Colloidal Sulphur and Selenium.—Julius Meyer.—To prepare colloidal sulphur and selenium solutions the powdered element is dissolved in a few cc. of hydrazine hydrate, and the solution is energetically shaken. When a saturated solution has been made a syrupy dark coloured liquid is obtained. If a few drops of this solution are added to some litres of water, stirring thoroughly with selenium, a red coloured solution is obtained, and with sulphur a whitish yellow solution. The selenium solution is exceedingly stable, and can be boiled for some time without undergoing any change. It can be kept for months. When it is allowed to stand for some time a small quantity of red selenium separates, but it disappears on shaking. The sulphur solution is not so stable as the selenium solution.

Isomeric Forms of Anhydrous Sodium Acetate.—D. Vorländer and Otto Nolte.—Two isomeric forms of anhydrous sodium acetate exist. The one which appears first when the amorphous melt cools may be called I., and the one appearing at a lower temperature II. The first is monoclinic and the second rhombic. II. passes over into I. at 198°; the transition is enantiotropic. When sodium acetate crystallises from absolute ethyl or methyl alcohol the salt II. is always obtained, whichever salt was originally dissolved. This salt II. is a very good condensation agent; it abstracts water more rapidly than I.

MEETINGS FOR THE WEEK.

Saturday, 27th.—Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner, D.Sc., F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2822.

THE RUSTING OF IRON IN WATER.

By W. A. BRADBURY.

Many years ago, Prof. Crace Calvert showed that bright iron rusted very quickly when immersed in Manchester tap-water, and he came to the conclusion that the carbonic acid and oxygen dissolved in the water was the cause of the rusting; the carbonic acid being the pre-disposing cause, as iron would not rust if carbonic acid was absent.

Since these experiments were made, a very considerable amount of attention has been given to the question, and many eminent authorities support Prof. Crace Calvert's conclusions.

As any experiments bearing on this subject have a certain value I wish to record the following:—Two flasks were filled with well boiled Manchester tap-water, and some coils of bright iron binding wire added; the flasks were then corked. No rust formed. A coil of bright iron wire, placed in water as drawn from the tap, soon became coated with rust, and the water then gave a blue coloration when tested with potassium ferrocyanide.

An experiment was arranged as per sketch, Fig. 1. A small flask containing water and iron wire was placed in a beaker, and water filled into the beaker until it rose partly up the neck of the flask. A small beaker was then wedged into position, so that the mouth of the small beaker was sealed. In a few hours the iron began to rust, and the rusting continued until a very fair amount was formed; the water gradually rose in the covering beaker until about one-fifth of the space was occupied by the water. The rust was filtered off from tbe water; a portion of the filtrate tested with potassium ferricyanide gave a blue coloration showing the presence of ferrous iron. The remaining portion of the filtrate was boiled; it turned usty-looking, and gave a deposit of oxide of iron; this was filtered off, and the filtrate was found to be free from iron.

The dissolving of iron by carbonic acid should give rise to an evolution of hydrogen,—

$$Fe + 2H_2CO_3 = FeH_2(CO_3)_2 + H_2$$

Apparatus arranged as per sketch, Fig. 2, using Manchester water and bright iron wire. In about five hours the water turned rusty-looking, but no gas had collected. The action was allowed to continue for a week, the formation of rust then seemed to cease. No gas had collected. In this case only a very slight amount of bicarbonate of iron was contained in the water.

To account for the absence of hydrogen in the collecting tube we must assume that nascent hydrogen combines with a portion of the oxygen dissolved in the water, and the rusting ceased when all this oxygen was used, and the water being sealed from atmospheric action no further supply of oxygen could be obtained.

As in the act of rusting the carbonic acid is again liberated, there should be a time when the liberated carbonic acid should act upon the iron and hydrogen be given off, all the oxygen having been used up.

As the amount of carbonic acid dissolved in water is usually very small, it may be that the hydrogen liberated in the final reaction is absorbed in the water, and hence its absence in the collecting tube.

To further test these points carbonic acid was passed into water for about fifteen minutes (170 cc. water), the arrangement, Fig, 2, being again used. After twenty-four hours action the iron remained perfectly bright; a portion of the water tested with potassium ferricyanide showed the presence of ferrous iron. No gas had collected Water was added to make up for the portion tested, and the experiment continued for six days. At the end of the sixth day the iron was still bright, and a bubble of gas had collected in the bend of the delivery tube. At the end of fourteen days the iron was still bright, and the delivery tube was filled with gas (about 5 cc.).

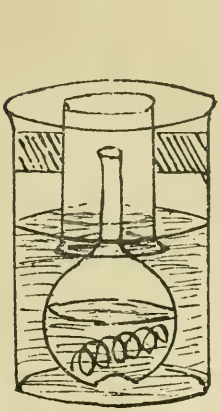


Fig. 1.

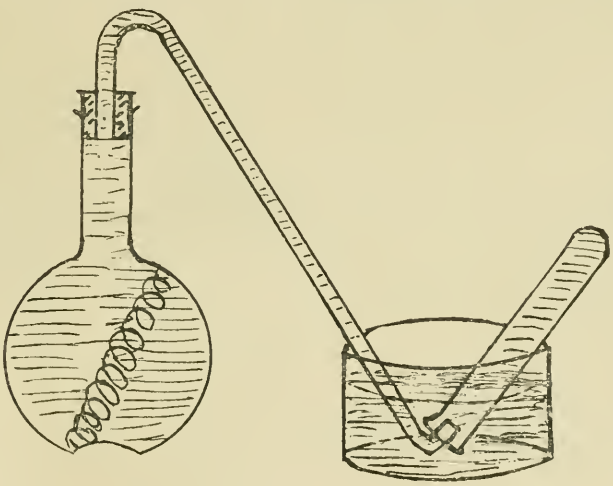


Fig. 2.

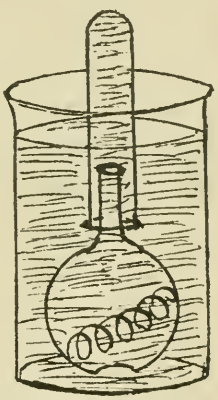


Fig. 3.

About three-fourths of the water, which was perfectly colourless and clear, was boiled; a large deposit of oxide of iron formed, consisting of both ferrous and ferric oxides. This was filtered off, and the filtrate evaporated to a small bulk; no further deposit occurred, and the liquid remained perfectly colourless on addition of potassium ferrocyanide.

The remaining one-fourth of the water with the iron still immersed in it was exposed to the atmosphere; in about two hours the water turned rusty-looking.

In this experiment we have a large amount of iron passed into solution, and the iron remaining perfectly bright, and the water remaining perfectly clear. This can only be due to the nascent hydrogen formed by the solution of the iron in carbonic acid, and no gas collected until all the oxygen dissolved in the water had been eliminated

The carbonic acid in the water was then present in sufficient quantity to give off more hydrogen, by its action on the iron, than the water was able to absorb.

The continuous rusting which goes on when the vessels are left open to the atmosphere is due to the ease with which oxygen from the atmosphere is absorbed by the water.

These experiments confirm the view that the rusting of iron in water is due to the dissolved oxygen and carbonic acid. They also show that the dissolved oxygen is utilised in two ways:—(1) It combines with the nascent hydrogen to form water, and (2) it decomposes the bicarbonate of iron to form rust, and however much rusting goes on there always remains in solution some bicarbonate of iron.

There seems to be a general impression that magnesium chloride in water has a strong corrosive action upon iron. It has been stated that magnesium chloride, *even in the cold*, acts in the following way:—

$$MgCl_2 + Fe + 2H_2O = Mg(OH)_2 + FeCl_2 + H_2.$$

To 500 cc. of well-boiled water 25 cc. of a saturated solution of magnesium chloride was added, and bright iron wire placed in the flask, using the arrangement Fig. 3. No signs of rust appeared, and not a bubble of gas collected after fifteen days action. On testing the solution with potassium ferrocyanide no blue coloration formed.

The arrangement, Fig. 2, was again used with boiled water and magnesium chloride. The solution was kept just short of ebullition by heating the flask on a sand-bath. After twenty-four hours heating neither rust nor gas had formed. The solution was evaporated to a small bulk, and it was found to be free from either ferrous or ferric iron.

This experiment was repeated, using a saturated solution of magnesium chloride. No gas formed, no iron dissolved. Magnesium chloride then does not act upon iron, either in the cold or heat at atmospheric pressure.

Dr. J. Grossman, in a paper read before the Society of Chemical Industry in Manchester, says that in the presence of carbonate of lime which most natural waters contain, magnesium chloride does not corrode iron when heated to a pressure of 200 lbs. or 300 lbs. per square inch.

We must therefore conclude that magnesium chloride has not the deleterious action upon iron which is usually ascribed to it.

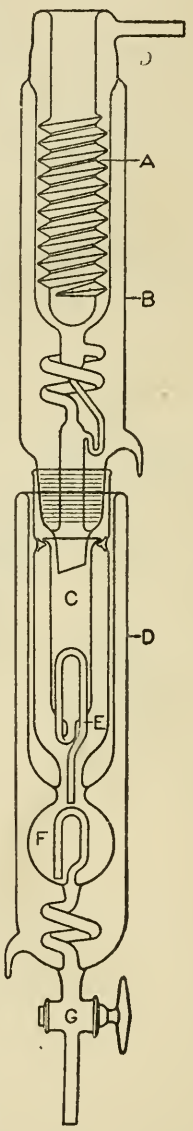
ON EXTRACTION WITH LIQUEFIED GASES AND THE AMMONOLYSIS OF HYDRAZINE SULPHATE.

By FRITZ FRIEDRICHS.

In connection with the choice of a solvent for use in extraction two considerations are of importance:—First, the relative solubility of the substances to be separated, and, second, the ease with which the solvent may be recovered without loss and without decomposition of the extract or of the residue. Since the removal of the solvent is usually effected by evaporation, a solvent with the lowest possible boiling-point would normally be preferable, especially when the material to be extracted decomposes at relatively low temperatures or possesses a high vapour tension. This leads at once to the application of liquefied gases in extraction in case the usual solvents cannot be readily recovered after the operation is complete.

The reason that such comparatively inexpensive gases as ammonia, sulphur dioxide, hydrogen sulphide, methylamine, &c., have not found more frequent application as extracting media in scientific and industrial work lies in the fact that the solvent power of these substances, with the exception of ammonia, has not yet been thoroughly investigated, and, further, that suitable apparatus for the purpose has not yet been designed. Various extractions, to be discussed in more detail later, have already been carried out by A. W. Browne, T. W. B. Welsh (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1728), and A. E. Houlehan (*Ibid.*, 1911, xxxiii., 1734), but the apparatus employed has not yet been completely developed for general use. The author of the present paper, in undertaking the continuation of the work, has consequentiy devised, on the basis of the work already done, the apparatus shown in the accompanying sketch.

The apparatus consists of three parts—(1) the extraction apparatus proper, D, (2) the container C, for the substance to be extracted, suspended in D from three glass projections, and (3) the condenser B, which is carefully ground to fit D. The extraction apparatus is modelled after the Landsiedl device, except that the bulb F is provided with a small syphon and with a stopcock, G, through which the extract may be drawn off, and that the entire apparatus is insulated by means of a vacuum jacket. Between this jacket and the inner part of the apparatus a small quantity of the refrigerant may be introduced. The condenser is of the screw type (*Zeit. Angew. Chem.*, 1910, xxiii., 2425), the screw itself constituting a receptacle for the refrigerant, and is, like the extraction apparatus, surrounded by a vacuum jacket. In order to permit free delivery of the condensate and free return of the vapours the condenser is equipped with a special device clearly shown in sketch. It is to be noted that the glass tubes passing through the vacuum jackets are in each case so constructed as to permit thermal expansion or contraction without breaking the apparatus. The upper part of the condenser is provided with an inlet tube for the gas to be liquefied, which is obtained from some convenient source, either a cylinder or a gas generator, and which is suitably purified and dried (in the case of ammonia, for example, by means of a long tube filled with sodium wire). It is advisable also to connect the condenser with a mercury manometer, which serves the double purpose of indicating the pressure in the apparatus and of acting as a safety outlet.



For the gases already named, solid carbon dioxide and ether may be used as the refrigerant, while for gases with lower boiling-points, such as oxygen or methane, liquid air may be employed. When liquid air is used it is advisable to introduce first a small amount of ether into the apparatus, and then slowly to add the liquid air, in order to minimise danger of breaking the apparatus. In order to obtain still lower temperatures in the condenser, the screw may be connected with an air-pump, and the refrigerant caused to evaporate under reduced pressure.

The apparatus just described has been found to serve admirably in a research upon the ammonolysis of hydrazine sulphate. As already shown by Browne and Welsh, hydrazine sulphate is decomposed by liquid ammonia into free hydrazine and ammonium sulphate in accordance with the equation:—

$$N_2H_4.H_2SO_4 + NH_3 \rightleftarrows (NH_3)_2.H_2SO_4 + N_2H_4.$$

The reaction is, moreover, to be regarded as reversible, inasmuch as Lobry de Bruyn has already shown that free hydrazine can liberate ammonia from ammonium sulphate (*Rec. Trav. Chim.*, 1896, xv., 179). Since ammonium sulphate—or rather, in accordance with the hitherto unpublished experiments performed by Mr. L. J. Ulrich in the Cornell University Laboratory, the triammonate of ammonium sulphate—is entirely insoluble (Franklin and Kraus, *Am. Chem. Journ.*, 1898, xx., 820) in liquid ammonia, while hydrazine is comparatively soluble, the employment of an excess of ammonia during the extraction displaces the equilibrium toward the right, with the result that quantitative ammonolysis takes place. It was therefore to be expected, as Browne, Welsh, and Houlehan have already intimated, that anhydrous hydrazine might be conveniently prepared by this method.

The hydrazine sulphate used in the following experiments was obtained by precipitation with alcohol from an aqueous solution of a sample of the salt previously purified by four-fold re-crystallisation. This product was repeatedly washed with alcohol, and was finally dried in a desiccator. A weighed sample of this pure white salt was introduced into the vessel C in a Schleicher and Schüll extraction thimble, and after opening the stopcock G, the air was driven from the apparatus by means of ammonia. By filling the tube between the stopcock G and the bulb F with mercury, which is of course a good conductor of heat, it was found possible to supply automatically an amount of heat sufficient to effect continuous evaporation of the liquid ammonia in F. After the salt had become pretty well saturated with ammonia at room temperature, solid carbon dioxide and ether were introduced into the jacket of the extraction apparatus and into the condenser screw A. Ammonia was at once condensed, and the extraction began to take place. During this operation the bulk of the salt increased to such an extent that during the earlier experiments the paper thimble, and on one occasion even the vessel C, burst, while in another case C became clogged so as to necessitate interruption of the experiment. It was then found that these difficulties could be readily avoided by placing glass-wool in the thimble with the salt, by supporting the thimble upon a porcelain Witt plate, and by inserting several short pieces of glass tubing between the thimble and the walls of C. When the bulb F had become about three-fourths filled with liquid, the valve of the ammonia cylinder was closed. The operation of the apparatus was then entirely automatic, and was surprisingly smooth and uniform, as could be observed from the manometer. As the temperature of the gas that rises from F to the condenser is never higher in the apparatus than the boiling-point of liquid ammonia ($-33{\cdot}45°$ under atmospheric pressure) or of the liquid ammonia solution, the consumption of carbon dioxide is relatively low. During the ammonolysis experiments, for example, it was found necessary on the average to fill the condenser screw from three to four times for each extraction. After the extraction had been completed the apparatus was allowed to warm up and the gas to escape through the safety outlet. The extract was then drawn off by opening the stopcock G. When it was desired to measure the amount of the extract directly it was, of course, necessary to rinse out the bulb F with liquid ammonia. The vessel C containing the residual ammonium sulphate combined with considerable amounts of ammonia in the form of an ammonate was now removed, was left in a desiccator over sulphuric acid until free from ammonate ammonia, and was weighed. The results obtained in several typical experiments are summarised in the accompanying table.

In Experiments 2, 3, and 4 the presence of hydrazine in the residue could not be detected with the aid of Fehling's solution, nor could the presence of sulphuric acid be shown in the extract. In Experiment 1 several hard lumps of salt containing a considerable amount of hydrazine were found at the bottom of the thimble, indicating that the extraction was not in this case complete. This first experiment was therefore left out of account in calculating the average. The loss of hydrazine was occasioned by the necessity of rinsing out F with liquid ammonia.

	$N_2H_4.H_2SO_4$	$(NH_3)_2.H_2SO_4$.			NH_4.	
No. of expt.	used. Grms.	Obtained. Grms.	Calculated. Grms.	Per cent of theory.	Obtained. Grms.	Per cent of theory
1	2·082	2·14	2·11	101·4	—	—
2	2·366	2·42	2·43	99·6	0·529	90·6
3	4·688	4·79	4·76	100·6	0·817	95·9
4	8·377	8·52	8·50	100·2	—	—
Average of expts. 2, 3, and 4 ..				100·1		

From these experiments it is evident, as was to be expected, that the ammonolysis may be considered to proceed quantitatively under the prevailing conditions. It is further to be concluded that it should be possible without difficulty to prepare anhydrous hydrazine in larger amounts by this method. For this purpose it would, of course, be advisable to substitute an apparatus built of iron for that of glass. It would then be possible to use ice as the refrigerant, as the apparatus would readily bear a pressure of 4·2 atmospheres. The greater solvent power of liquid ammonia at the higher temperature would undoubtedly be of advantage. Experiments in this direction are now in progress.

It is hoped that this illustration of the application of liquefied gases as extraction media will call the attention of other investigators to this field of work, and that the apparatus described herewith may be of service in carrying out further experiments.

In conclusion the author wishes to express his gratitude to Prof. A. W. Browne, who has suggested the present investigation, and to the firm of Grenier and Friedrich, Sütterbach, Germany, by whom the apparatus has been constructed.—*Journal of the American Chemical Society*: xxxv., No. 3.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Concluded from p. 298).

9. *Ammono Salts Analogous to the Zincates, Aluminates, Plumbites, &c.*—Among the phenomena with which the student of chemistry early becomes familiar is the solubility of certain metallic hydroxides, such as the hydroxides of aluminium, lead, and zinc, in solutions of the alkali hydroxides, and he soon learns to write confidently the equations—

$$Al(OH)_3 + 3KOH = Al(OK)_3 + 3H_2O,$$
$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O,$$
$$Pb(OH)_2 + 2KOH = Pb(OK)_2 + 2H_2O,$$

as representing the reactions which take place. As a matter of fact, the composition of the compounds thus formed is still a matter of doubt (Hantzsch, *Zeit. Anorg. Chem.*, 1902, xxx., 289; Wood, *Journ. Chem. Soc.*, 1910, xcvii., 878).

The observations that certain metallic salts in solution in liquid ammonia, when treated with potassium amide, give precipitates which re-dissolve on adding the precipitant in excess, suggested the possibility of preparing the ammonia analogues of the substances supposed to be present in the alkaline solutions mentioned above. The results of work in this direction have been highly satisfactory; for most of the compounds so far obtained are beautifully crystalline and of sharply definite composition; results which are in striking contrast to the properties of the analogous oxygen compounds in this respect.

After the earlier unsatisfactory attempts to prepare a potassium ammonoplumbite (Franklin, *Journ. Am. Chem.*

* From *American Chemical Journal*, xlvii., No. 4.

Soc., 1905, xxvii., 843), the first representative of this class of compounds to be obtained, namely, potassium ammonozincate, was successfully prepared by F. F. Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 660); Franklin, *Ibid.*, 1907, xxvii., 1274).

Potassium Ammonozincate, $Zn(NHK)_2.2NH_3$.—In view of the fact that metallic zinc dissolves in aqueous potassium hydroxide with the evolution of hydrogen, it was hoped that analogously a pure solution of potassium ammonozincate would be formed by the action of a liquid ammonia solution of potassium amide on the metal. Fitzgerald found that the reaction represented by the equation $Zn+2KNH_2 = Zn(NHK)_2+H_2$ takes place readily enough, especially if the zinc is alloyed with a little platinum. Because, however, of the slight solubility of the salt in liquid ammonia, its separation from the excess of zinc is a matter of considerable difficulty.

A second method by which potassium ammonozincate has been successfully prepared is by treating zinc amide (Fitzgerald, *loc. cit.*), obtained by the action of ammonia gas on zinc ethyl, with a liquid ammonia solution of potassium amide. The amorphous insoluble zinc amide formed by the action of ammonia on zinc ethyl is converted into a mass of well crystallised potassium salt when allowed to stand overnight in contact with an excess of a solution of potassium amide. The reactions involved are represented by the equations—

$$Zn(C_2H_5)_2+2NH_3 = Zn(NH_2)_2+2C_2H_6$$

and

$$Zn(NH_2)_2+2KNH_2 = Zn(NHK)_2.2NH_3.$$

Finally, and most conveniently, the salt has been prepared by the action of an excess of potassium amide in solution in liquid ammonia directly upon ammonated zinc iodide, as represented by the equation—

$$ZnI_2.4NH_3+4KNH_2 = Zn(NH_2)_2.2KNH_2+2KI+4NH_3.$$

The crop of well crystallised slightly soluble zincate thus formed is easily obtained pure by washing with liquid ammonia to remove the potassium iodide formed, together with the excess of potassium amide. Potassium ammonozincate dissolves readily in liquid ammonia solutions of ammonium nitrate (that is to say, in nitric acid). It is energetically hydrolysed by the action of water; even short exposure to the action of the moisture of the atmosphere produces a superficial sticky layer on the clear dry crystals. It is not explosive. When heated *in vacuo* potassium ammonozincate remains intact up to 160°; as the temperature is increased beyond this point, the substance melts and gives off ammonia. Heating the salt for some hours at temperatures between 250° and 300° gave a residue of approximately the composition represented by the formula $Zn(NHK)_2.\frac{1}{3}NH_3$.

Potassium Ammonostannate, $Sn(NK)_2.4NH_3$ and $Sn(NK)_2.NH_3$.—The preparation of a pure crystalline salt of the composition represented by the first formula was accomplished by Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 1694) by the action of potassium amide in excess on a liquid ammonia solution of stannic iodide. The reaction takes place in accordance with the equation $SnI_4+6KNH_2 = Sn(NK)_2.4NH_3+4KI$ (stannic iodide forms a white addition product with ammonia), and since the salt formed is crystalline and but slightly soluble in ammonia, it is easily washed free from potassium iodide and excess of potassium amide. Potassium ammonostannate is soluble in liquid ammonia solutions of ammonium iodide; that is to say, it is decomposed and dissolved by hydriodic acid in liquid ammonia solution. It is vigorously attacked and decomposed by water. Heated in contact with the air it takes fire and burns with brilliant incandescence. It is not explosive. When heated *in vacuo* it loses 3 molecules of ammonia and is converted into a brick-red powder of the composition represented by the formula $Sn(NK)_2.NH_3$.

It is most interesting to point out the analogies between these two ammono compounds and the correspondin oxygen salts. A formula for potassium metastannate cannot be given corresponding to the formula $Sn(NK)_2.4NH_3$, but if the nitrogen compound be given any one of the formulæ $(NH_2)_2$:Sn:$(NHK)_2.2NH_3$, $(KNH)_2$:Sn:$(NHNH_4)_2$, or $Sn(NH_2)_4.2KNH_2$, then it is easy to write the analogous formulæ $(HO)_2$:Sn:$(OK)_2.2H_2O$, $(KO)_2$:Sn:$(OH_3O)_2$, and $Sn(OH)_4.2KOH$ for the oxygen compound (*cf.*, Bellucci and Parravano, *Zeit. Anorg. Chem.*, 1905, xlv., 142). If Bellucci's contention that the formula for the ordinary trihydrate of potassium metastannate is to be written $K_2Sn(OH)_6$, then analogously the formula for the ammonostannate may be written $K_2Sn(NH_2)_6$. Corresponding to the formula, $K_2SnO_3.3H_2O$, usually given to the aquo salt, the formula $K_2Sn(NH)_3.3NH_3$ may be written for the ammono salt.

The similarity of the behaviour of these two compounds when heated is also noteworthy, for just as the aquo salt loses 3 molecules of water, so the ammono salt loses 3 molecules of ammonia, to form compounds which in the one case may be given either of the formulæ K_2SnO_3 or O:Sn:$(OK)_2$, and in the other any one of the three formulæ $K_2Sn(NH)_3$, NH:Sn:$(NHK)_2$, or $Sn(NK)_2.NH_3$ (Note 10).

Potassium Ammonocadmiate, $Cd(NHK)_2.2NH_3$ (Note 11).—When a solution of potassium amide is added to ammonated cadmium iodide or nitrate, an amorphous or microcrystalline insoluble product is obtained which analysis shows to be a cadmium salt corresponding in composition to the zinc salt described above (Note 12).

Potassium Ammonoplumbite, $PbNK.2\frac{1}{2}NH_3$, $PbNK.2NH_3$, and $PbNK.NH_3$.—The attempts mentioned above to isolate the product of the action of potassium amide on lead imide have recently been renewed in this laboratory and with entire success (*Journ. Phys. Chem.*, 1911, xv., 509). It has been shown that the reaction between the ammono base and the amphoteric imide is to be represented by the equation $PbNH+KNH_2 = PbNK+NH_3$. The salt possesses conspicuous crystallising power and is obtained from very concentrated solutions in the form of beautifully developed colourless transparent crystals, having the composition represented by the formula $PbNK.2\frac{1}{2}NH_3$. At 40° below zero, if the pressure is sufficiently low, the salt effloresces, losing one-half a molecule of its ammonia. At 60° it loses an additional molecule of ammonia, and is converted into a dark brown mass still showing the form of the original crystals. The product thus formed, $PbNK.NH_3$, does not further lose ammonia when heated to a temperature of 140°. At somewhat higher temperatures the compound explodes. It also explodes violently when brought into contact with water or dilute acids, and occasionally even on simple exposure to the atmosphere.

When a solution of ammonium iodide in liquid ammonia is gradually added to a solution of potassium ammonoplumbite, a brown precipitate of lead imide is first formed, which with further addition of ammonium iodide is converted into a white ammonobasic lead iodide (see Section 10). On adding still further quantities of ammonium iodide, the basic lead salt dissolves to form lead iodide. The equations representing these reactions are as follows:—

$$PbNK+NH_4I = PbNH+KI+NH_3,$$

$$2PbNH+NH_4I = NH_2PbNHPbI.NH_3,$$

and

$$PbNPbI.2NH_3+3NH_4I = PbI_2+6NH_3.$$

Conversely, the gradual addition of potassium amide to a solution of lead iodide brings about the successive formation of ammonobasic lead iodide, lead imide, and potassium ammonoplumbite.

The analogy between these reactions and those which result from the gradual addition of nitric acid to a solution of potassium plumbite, and the inverse reactions which accompany the gradual addition of potassium hydroxide solution to a solution of lead nitrate, are so obvious as to require no statement in detail.

Potassium Ammonocuprite, $CuNK_2 2\frac{1}{2}NH_3$ and $CuNK_2.NH_3$.—When cuprous nitride, obtained in the manner described by Fitzgerald (*loc. cit.*), is treated with a liquid ammonia solution of potassium amide, a salt of the composition represented by the first of the above formulæ is formed, which, because of its extreme solubility, has so far been obtained only in an approximate degree of purity (experimental results not published). At low temperatures the salt separates from very concentrated solutions in the form of colourless crystals, which readily part with one and one half molecules of their ammonia of crystallisation. One molecule of ammonia is retained up to 200°, above which temperature the heating has not been carried.

The formation of potassium ammonocuprite is represented by the equation $Cu_3N + 6KNH_2 = 3CuNK_2 + 4NH_3$.

Potassium Ammonothallate, $TlNK_2.4NH_3$, $TlNK_2.2NH_3$, and $TlNK_2.1\frac{1}{2}NH_3$.—Black thallium nitride dissolves in liquid ammonia solutions of potassium amide to form a clear yellow solution, from which, on cooling the not too dilute solution, a crop of beautiful yellow crystals separates. Dried *in vacuo* at −40°, these crystals retain their colour and have been shown to have the composition represented by the formula $TlNK_2.4NH_3$ or $TlNH_2.2KNH_2.2NH_3$ (experimental results not yet published). On warming up to laboratory temperature the salt takes on a lighter colour, loses 2 molecules of ammonia, and is converted into a compound which is represented by the formula $TlNK_2.2NH_3$ or $TlNH_2.2KNH_2$. When heated to 100° the latter compound loses two-ninths of its nitrogen in the form of ammonia and is converted into a black mass to which the formula $TlNK_2.1\frac{1}{2}NH_3$ may be given, but which may be merely a mixture of thallium nitride and potassium amide in the proportions represented by the formula $Tl_3N.6KNH_2$. When dry, that is, when free from liquid ammonia, any one of these products explodes with violence on the slightest provocation. The yellow solution of potassium ammonothallate, when treated with a solution of ammonium nitrate, gives first a precipitate of thallium nitride, which then, on further addition of the acid, goes into solution as thallium nitrate.

10. *Ammonobasic Salts. Ammonolysis.*—As has already been shown, the reactions between ammonia and the non-metallic compounds indicated in the equations given above (p. 296) are strictly analogous to those which take place when the respective substances are treated with water, and are therefore appropriately designated as ammonolytic in order to recall their close relationship to hydrolytic reactions. These particular ammonolytic reactions proceed energetically to completion and are quite as irreversible as are the corresponding reactions which result from the treatment of the halogen compounds of the non-metals and water. Silicon chloride and the phosphorus chlorides, for example, are completely ammonolysed in contact with ammonia, just as they are completely hydrolysed by the action of water. However, just as certain well known hydrolytic reactions are reversible, so also have salts of a number of the less positive metals, when treated with liquid ammonia, been found to give basic precipitates which are increased in amount by the addition of potassium amide, and which are completely dissolved by the addition of an appropriate acid, that is to say, by the addition of an ammonium salt.

Attention was first called to the existence of such reactions by Franklin and Cady (*Journ. Am. Chem. Soc.*, 1904, xxvi., 512), who observed the formation of what they assumed to be a "basic bismuth nitrate" ("a salt related to ammonia as the ordinary basic nitrate is related to water") around a bismuth anode during the passage of an electric current through a dilute solution of ammonium nitrate in liquid ammonia.

Franklin and Kraus (*Am. Chem. Journ.*, 1900, xxiii., 299) had earlier observed the separation of a small quantity of an insoluble compound accompanying the action of liquid ammonia on mercuric chloride. It was later shown that the formation of this residue is due to the ammonolytic action of liquid ammonia on mercuric chloride (Franklin, *Journ. Am. Chem. Soc.*, 1905, xxvii., 841), as represented by the equation—

$$HgCl_2 + 2NH_3 \rightleftarrows NH_2HgCl + NH_4Cl,$$

and that the product is identical with the well known infusible white precipitate. The reversibility of the reaction is shown by the observation that addition of ammonium chloride to the mercuric chloride prevents the formation of the white precipitate when the mixture is treated with liquid ammonia, and by the fact that addition of sodium amide to the system represented by the above equation displaces the equilibrium to the right, while addition of ammonium chloride solution to the liquid in contact with the precipitate determines the disappearance of the latter.

In an entirely similar manner, lead nitrate, lead iodide, mercuric iodide, mercuric bromide, bismuth iodide, bismuth bromide, and stannic iodide undergo ammonolysis to a greater or less extent when treated with liquid ammonia. Although abundantly soluble in liquid ammonia no one of those salts dissolves to a clear solution unless a quantity of an appropriate ammonium salt is present.

The observations of Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 1695) on the behaviour of stannic iodide in solution in liquid ammonia are especially illuminating in this connection. When a limited quantity of liquid ammonia is brought into contact with stannic iodide to which a minute quantity of ammonium iodide has been added, the tin salt dissolves to form a dense colourless and clear solution. When additional ammonia is distilled into the tube in such a manner as not to mix its contents, the separation of a white precipitate is observed, occupying a zone between the concentrated solution of the stannic iodide and the freshly distilled ammonia. On shaking the tube and thus mixing its contents the precipitate disappears. On again distilling ammonia into the tube, the precipitate reappears, to disappear again on shaking the tube. The separation of the precipitate may be observed several times by repeating the operations thus described. After a relatively large amount of liquid ammonia had been added, the precipitate becomes permanent, and the separation of tin from the solution is complete, as is shown by the observation that the addition of potassium amide to the supernatant solution fails to produce any further precipitation. The addition of any considerable quantity of ammonium iodide to the solution in the beginning prevents the ammonolysis of the salt. Whether in this particular instance the product of ammonolysis is an ammonobasic salt, or an amide, imide, or nitride of tin, free from iodine, has not been determined. The remarkably close parallelism between the phenomena just described and the familiar action of water on acid solutions of antimony chloride and bismuth chloride is so obvious as to require no further comment.

The ammonobasic salts of definite composition which have so far been obtained are the ammonobasic mercuric halides of the respective formulæ $NH_2—Hg—Cl$, $Hg:N—Hg—Br$, and $Hg:N—Hg—I$, and the ammonobasic lead iodide of the formula $Pb:N—Pb—I.2NH_3$. The reactions whereby these compounds have been obtained are represented by the equations—

$$HgCl_2 + 2NH_3 = NH_2—Hg—Cl + NH_4Cl,$$
$$2HgBr_2 + 4NH_3 = Hg:N—Hg—Br + 3NH_4Br,$$
$$2HgI_2 + 4NH_3 = Hg:N—Hg.I + 3NH_4I,$$
$$2PbI_2 + 6NH_3 = Pb:N—Pb—I.2NH_3 + 3NH_4I,$$

the amount of ammonobasic salt formed being increased to a reasonable yield, when desired, by the addition of limited quantities of potassium amide.

The ammonobasic salts which have thus been obtained as definite chemical compounds, as well as the others described above as having been observed qualitatively, all appear as insoluble amorphous precipitates (Note 13), characteristics which, as is well known, attach to the more familiar aquobasic salts. Even the tendency of the latter class of products to form basic mixtures of more or less indefinite composition is exemplified in the failure of

attempts (Franklin, *Journ. Am. Chem. Soc.*, 1905, xxvii., 849) to obtain ammonobasic compounds of definite composition from either aluminium of antimony iodide. In the case of antimony iodide it is interesting to note that continued agitation, through several weeks, of the finely divided salt with liquid ammonia—which, as the ammonia abstracted iodine from the salt in the form of ammonium iodide, was from time to time replaced by fresh solvent—failed, in the hands of Fitzgerald, to yield a compound of definite composition.

In addition to the compounds of mercury, two other representatives of the class of ammonobasic salts are found described in the literature. The ammonobasic titanium halides represented by the formulæ N≡Ti—Cl and N≡Ti—Br have been prepared by Ruff and Eisner (*Ber.*, 1908, xli., 2250) by the action of liquid ammonia on the chloride and bromide of titanium respectively.

11. *Ammonobasic Mercuric Salts.* — The formation of the ammonobasic mercuric salts NH_2—Hg—Cl, Hg:N—Hg—Br, and Hg:N—Hg—I by the ammonolysis of mercuric chloride, bromide, and iodide respectively in liquid ammonia solution are facts which have an important bearing upon the question of the constitution of the large group of the so-called mercuriammonium compounds, a question which has never received a satisfactory answer.

Since these ammonobasic mercuric salts, the preparation and description of which have been given in a previous paper (*Journ. Am. Chem. Soc.*, 1905, xxvii., 838), cannot be distinguished from the respective products of the action of aqua ammonia on the mercuric halides, it follows that the latter compounds are identical with the former. It is therefore altogether wrong to formulate the ammonobasic mercuric chloride, NH_2—Hg—Cl, as a double salt of dimercuriammonium chloride and ammonium chloride, Hg_2N^{v}—Cl.NH_4Cl, and the ammonobasic iodide, Hg:N—Hg—I, as dimercuriammonium iodide, Hg_2N^{v}—I, as is done in the majority of the dictionaries and handbooks of chemistry.

In a subsequent paper the attempt will be made to show that all the mercury ammonia compounds described in the literature, instead of being ammonium salts in which ammonium hydrogen is substituted by mercury—as the various mercuriammonium theories assume them to be—are, as a matter of fact, either normal mercuric salts with ammonia of crystallisation, or basic products resulting from ammonolysis, or both ammonolysis and hydrolysis, of the normal mercuric salts.

Conclusion.

It has been shown in this paper that an ammonia system of acids, bases, and salts may be formulated on the basis of ammonia as the typical substance, and in a manner entirely analogous to the formulation of the ordinary oxygen acids, bases, and salts as derivatives of water. In other words, a system of acids, bases, and salts has been developed in which nitrogen occupies a position similar to that occupied by oxygen in the system of Lavoisier.

The acids of the ammonia system are the acid amides and imides, including the amides and imides of the non-metallic elements; the bases of the system are the metallic amides and imides; the salts are the metallic derivatives of the acid amides and imides.

In order to emphasise their relations to ammonia, and for convenience in discussing the reactions between representatives of the ammonia system, these acids, bases, and salts are referred to as ammono acids, ammono bases, and ammono salts respectively.

Reactions in liquid ammonia solutions which are strictly analogous to the familiar hydrolytic reactions in water solutions have been discovered and are accordingly designated as ammonolytic reactions. Products which have been named ammonobasic salts are shown to result from the smmonolysis of certain salts of the heavy metals.

It is shown in this paper that the relationships indicated by this system of nomenclature are by no means purely formal. The ammono acids exhibit certain truly acid properties, the ammono bases react in liquid ammonia solutions in a manner strictly analogous to the familiar reactions of the ordinary bases in aqueous solutions, and the ammono salts are as certainly salt-like compounds as are the products of the interaction of ordinary acids and bases.

A considerable number of new representatives of the ammonia system of acids, bases, and salts have been made by means of reactions carried on in liquid ammonia solutions, and are found described in the above pages.

Notes.

10. Howe, *Journ. Am. Chem. Soc.*, 1909, xxxi., 259, first called attention to the remarkable analogies between these aquostannates and ammonostannates.

11. Prepared in the laboratory of Stanford University by G. S. Bohart. Results not yet published.

12. It is interesting to note in this connection that cadmium hydroxide has not been observed to possess amphoteric properties.

13. In two tubes containing mercuric chloride and liquid ammonia which were sealed up six or eight years ago, the white, apparently amorphous precipitates of NH_2HgCl which separated at that time have changed into aggregates of well developed crystals.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A Mercury-bath Level.

Up till now it has generally been necessary to employ a spirit-level for transportable instruments. The best level is that which is formed by the reflexion in a bath of mercury, but the extreme mobility of the surface of this bath has limited its employment to observatory instruments. Only in the prismatic astrolabe has the difficulty been got over by the use of baths of amalgam, but this has also very serious disadvantages. Messrs. André Broca and Florian have managed to contrive an apparatus that has been realised by the Lacour Duthiot establishments where the useful properties of the mercury-bath have been kept, while the production of waves on the surface has been suppressed by trepidations. This result is obtained by placing the mercury-bath in a box completely closed, and by surmounting it with glycerin. The upper part of the box, that is to say the top, is an objective in contact with the glycerin. With these elements an auto-collimative lunette is constituted, and it is possible with a focal distance of 18 c. and an objective with an opening of 28 mm. to regulate the horizontality to about a fraction of a second. The apparatus also does not take up much space, as the lateral walls of the mercury-box have been formed by a spherical zone in which the mercury is raised till on the level at which the tangent plane makes, with the horizon, an angle equal to the angle of the meeting point of the mercury with the top of the box; this suppresses the perturbations of the surface caused by the meniscus, and thus the bath may have a diameter very slightly superior to that of the objective. This apparatus may be used as a seismograph, and if it is made of sufficiently large dimensions, it may also be possible to study with it the perturbations of the vertical.

Volcanic Gases.

In a notice analysed by M. Lacroix, Professor at the Natural History Museum, Messrs. Day and Shephers conclude from experiments made at Mount Kilanea, that amongst the volatile products emanating from lava in fusion, at a temperature of about 1100°, there is to be found an abundance of water-vapour, which has been condensed and studied. This is a confirmation of the observations

made in 1865 at Etna by Fouqué and Silvester. If other observers, as Messrs. Brun and Green, have concluded from other observations made at Kilanea, that the exhalation is dry, it is because they have operated, not on the gases emanating from the lava in a state of fusion, but upon the gases collected near the edge of the crater. In this region of the volcano there is, indeed, a large amount of dehydrated gases and finely-divided sulphur. Prof. Armand Gautier confirmed the observations of his colleague.

The rôle of Heredity in Dogs.

M. Philippe de Vilmorin has undertaken some very curious experiments on the transmission of hereditary characteristics in dogs. M. Edmond Perrier, Director of the Paris Natural History Museum, has notified these experiments to the Academy of Sciences. There are several races of dogs that have no caudal appendage. Thus, the race of Bourbon brach dogs, the Auvergne brachs, the German brachs, the Spanish bretons, the Hungarian shepherd dogs, the long-haired loulous of the Scheldt boatmen have no tails. But is the characteristic hereditary? M. Philippe de Vilmorin has observed about a hundred individuals, and has made about twenty-seven crosses between dogs of different species. According as the dogs have or have not any caudal appendage. and according to the greater or less length of the same, M. de Vilmorin classes them in three categories. The terminology that is employed for the classification of the mollusca has served him for the designation of the canine categories. The Anoura dogs are characterised by the total absence of any tail. The Brachyura dogs have a short tail. The Macroura dogs have, on the contrary, a normal tail. Observation has shown that the character of having no tail dominates according to the law of Mendel. It would then seem that all dogs totally tailless are hybrids. On the contrary, the dogs that have a long tail are of a pure type. By crossing Anoura dogs with Macroura dogs half hybrids and half normal dogs have been obtained. By crossing, on the contrary, Anoura dogs amongst themselves, the dogs obtained without a tail were in the proportion of 75 per cent, and the dogs with a tail in the proportion of 25 per cent. These researches confirm once more the discovery made by Mendel about 1868, which discovery has lain dormant for so many long years. The glory of Mendel is quite recent. It was only forty years after the publication of his first studies concerning the transmission of hereditary characters that the Dutch botanist, Van Vries, in 1900, discovered the laws of Mendel. Mendel was a monk in a Moravian convent near Brünn. He was passionately fond of cultivating his garden, where he hybridised sweet-peas. It was in this way that he discovered the laws of hybridation. Published in a little local review, the *Bulletin de la Réunion Scientifique de Brünn*, these laws remained for a long time hidden. Since Van Vries rescued them from oblivion naturalists and scientists are continually exploring this marvellously rich way which has given many interesting indications concerning the mysterious and complex problems of heredity.

Natural Incubation and Artificial Incubation.

The comparative study of natural incubation and artificial incubation is somewhat difficult, as it can only be made during the season in which it is convenient to procure hatching hens. For this reason the experiments that M. Brechemin has made on this subject were effected during the months of March, April, and May; they concerned, on the one hand, three turkeys, three hens, who were each time charged with a hundred eggs; on the other hand, there was an artificial incubator with a reservoir of water kept hot by means of a little lamp. In this apparatus a hundred eggs were placed each month; naturally the eggs had previously been thoroughly looked through. The results were the following:—Natural incubation—242 fecundated eggs gave 158 chickens; artificial incubation —243 fecundated eggs gave 209 chickens. The experiments were continued by the comparison of artificial breeding and natural breeding, the food being the same for all the chicks. Those given over to the care of the hens and turkeys disposed of a surface of 4000 square metres of free air, whilst the artificial breeder was surrounded by only 600 square metres of ground situated in a place the front part of which was covered with glass. Three months after the eggs were hatched it was seen that there were only 75 chicks left out of the 158 brought up naturally, whereas there were still 194 out of the 209 brought up artificially; that is to say, a loss of more than 50 per cent out of the natural breeding and only 10 per cent out of the artificial breeding. All the same, it must be noticed that the loss is not so great for the natural breeding when the hens are kept in breeding boxes or in closed hen-houses. As a conclusion to be drawn from his trials, M. Brechemin considers that natural hatching and breeding can be indicated for small enterprises and for reproductive breeding broods because they give more vigorous subjects; artificial incubation and breeding must nevertheless be preferred for all breeding enterprises of any extent.

The Evolution of Sea fishing.

Several deep-water fish, of which the zoological museums possess but very few examples, have made their appearance on the Paris fish market. Large quantities of these fish are to be found in the Central Market during the winter months. According to M. Edmond Perrier, Director of the Natural History Museum, these curious facts are the consequence of the evolution of sea-fishing. The fishers now go further and deeper to seek for the fish that are rarely to be found near the coast. For some years past trawlers have been going to fish on the coasts of Portugal, and their nets descend to a depth of 200 metres. Dr. Jugeat, sanitary veterinary surgeon at the Central Market, has noticed many fish like the beryx, of a bright scarlet colour; the *brama*, the *zeides*, the *Dentus marocanus*, the ancient bramides, whose eyes are particularly developed on account of the weak light that penetrates into marine waters at a depth of 200 metres. Very few Parisians consider that they are often given fish to eat that up till now were considered as zoological curiosities.

A Year without any Spots on the Sun.

During the first two quarters of the year 1913 the brilliant surface of the sun remained completely free of spots. M. Guillaume, astronomer at the Observatory of Saint-Genis Laval, near Lyons, has continued his observations during the third quarter. M. Bailland, Director of the Observatory, in a communication in M. Guillaume's name, remarks that also during this period there have been hardly any spots; on the contrary, brilliant faculæ have been observed. Another astronomer of the Lyons Observatory, M. Hajolet, has remarked a certain increase in the stronger magnetic perturbations, which are the only ones that it is possible to observe. The year 1913 is remarkable on account of the absence of spots on the sun. Such a minimum has not been observed since 1810.

Is it Land or a New Island?

General Scholaksky, delegate from the Russian Government to the Conference on the Map of the World, has presented two communications—one concerning a new map, in relief, of Siberia; the other concerning an important discovery that has been made by the hydrographic officers of the Russian Navy instructed with the exploration of the Northern Siberian coast from Behring's Straits to the Tamur peninsula. These officers have discovered a new land, or a new long and narrow island, which extends towards the east as far as the longitude 97° twelve minutes of the Greenwich meridian. It is not yet known how far this land stretches towards the west. The latitude of it is 80° four minutes. It occupies about the same position as Spitzbergen and Franz-Josef's land. The mission has not yet returned from Kamschatka. This news has been transmitted by telegram.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the heavy loss the Society had sustained through death, during the vacation, of the following Fellows:—E. L. Barret, Paris; J. C. Bell, Manchester; A. Cantin, Mauritius; T. Crossman, Starbeck; J. Davidson, Holywell Green; L. M. Deane, Ilkley; Sir W. N. Hartley, Dublin; J. Lewkowitsch, W. Hampstead; H. Marshall, Dundee; I. Patchett, Batley; M. G. Roy, Chintadrepettah; A. Wallace, Agra.

The following announcement was made:—That, in future, a list of the papers to be read at each Ordinary Scientific Meeting will be advertised in the *Morning Post* on the Wednesday previous to the day of meeting.

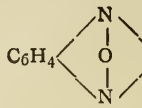
Messrs. C. K. Tinkler and E. Cahen were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Richard Watson Askew, B.A., Brierley, Chelmsford Road, Durban, Natal, South Africa; Sankar Rao B. Badami, M.A., Badami House, Hulsurpet, Bangalore, India; Stanley Charles Bate, B.Sc., 50, Alexandra Road, Upper Norwood, S.E.; Charles Maurice Berlein, B.A., Cross Oak, Berkhamsted; Arthur Bicknell, B.Sc., Balliol College, Oxford; Augustus Pearce Llewellyn Blaster, B.A., Chidham, Potters Bar, Middlesex; Adhor Krishna Bose, 90, Musjeed Baree Street, Calcutta, India; Arthur Bramley, B.Sc., 19, Cambridge Road, Barnes, S.W.; Arthur Joseph Brearley, B.A., 13, Victoria Terrace, Exeter; Bertram Campbell, B.Sc., Beechover, Manor Avenue, Grimsby; Frederick George Carter, Amritsar Distillery, Amritsar, Punjab, India; Santi Pada Chowdry, Economic Research Laboratory, Rewa State Industries, Umaria, India; Francis William Clark, 35, Wilmington Square, W.C.; Herbert Stoddard Coleman, 14, Dunsford Road, Bearwood Road, Smethwick; Thomas James Drakeley. B.Sc., 36, Mitchell Street, Newtown, Wigan; Cyril Duncan Fuller, 62, Hill Street, Totterdown, Bristol; Charles John Dickenson Gair, 39, Cranston Road, Forest Hill, S.E.; Stanton Gibson, B.Sc., 28, Lordship Park, N.; Richard Hargreaves, B.A., Chatburn, Clitheroe; George Alfred Hebden, 78, Norborough Road, Tinsley, Sheffield; Richard Pendarves Hodges, 42, Olive Road, Cricklewood, N.W.; William Francis Hollely, 67, Ross Road, Wallington, Surrey; Alexander Hynd, M.A., B.Sc., 196, Baldridgeburn, Dunfermline; William Johnson, B.Sc., Walton, Stoneygate Avenue, Leicester; Harold Bramfield Jones, Broadway House, Northolme Road, Highbury, N.; Gholam Rasal Khan, B.Sc., Lyallpur, Punjab, India; Sidney Oliver Leivesley, care of W. Leivesley, Esq., Chillagoe, N. Queensland, Australia; William John Lewis, 10, Lightoaks Road, Pendleton Manchester; Percival James Lycett, Castle Hill, Wolverley, Kidderminster; Frank Clifford Marchant, St. Kilda's, Manor Road, Forest Hill, S.E.; Kunerji Gosai Naik, M.A., B.Sc., Krishnath College, Berhampore, Dist. Murshidabad, Bengal, India; John Allen Nichols, Stanley Mount, New Mills, Stockport; John Thomas Pattison, 72, Bath Road, Southsea, B.O., Portsmouth; Wilfrid Roberts Powell, B.A., 14, Marlborough Road, Richmond, Surrey; Henry Edward Findlater Pracy, 25, Grosvenor Park, Camberwell, S.E.; John McArthur Stuart, Balliol College, Oxford; Robert Tennant, 4, Park Terrace, Queen's Park, Glasgow; Henry Walker, 10, Melrose Terrace, West Kensington Park, W.; Henry Wood, The Limes, 62, Culverden Road, Balham, S.W.

Of the following papers, those marked * were read:—

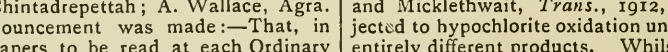
*266. "*The Conversion of Orthonitroamines into* iso-*Oxadiazole Oxides* (*Furoxans*)." By Arthur George Green and Frederick Maurice Rowe.

Whilst *o*-nitroaniline on alkaline hypochlorite oxidation is quantitatively converted into ben*zis*ooxadiazole oxide,—

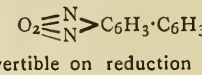


and 2 : 4.dinitroaniline (when an alcohol is present) into a chloromethoxy-(or ethoxy)ben*zis*ooxadiazole oxide, the presence of an amino-, acetylamino , azo-, or sulphonic group in the para-position occasions a complete disruption of the benzene ring, and only in the case of the sulphonic acid was a small quantity of a ben*zis*ooxadiazol oxide produced.

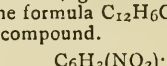
The two isomeric *o*-dinitrobenzidines (Cain, Coulthard, and Micklethwait, *Trans.*, 1912, ci., 2298), when subjected to hypochlorite oxidation under like conditions, yield entirely different products. Whilst the isomeride melting at 275° (regarded by these authors as 3 : 5′-dinitrobenzidine) produces a typical furoxan,—



readily convertible on reduction into a diphenoquinone tetraoxime, $C_6H_3(:NOH)_2{\cdot}C_6H_3(:NOH)_2$, and a bisben*zis*ooxadiazole,—



the isomeric *o*-dinitrobenzidine melting at 233°, regarded as the 3 : 3′-derivative, gives a reddish brown crystalline compound of the formula $C_{12}H_6O_4N_4$, which is probably an internal azo-compound.



The above bisben*zis*ooxadiazole oxide (bisbenzfuroxan) crystallises from chlorobenzene in pale yellow thin hexagonal plates, melting at 211°. The corresponding bisben*zis*ooxadiazole (bisbenzfurazan) forms yellow needles, which melt at 244°. The diphenoquinonetetraoxime is a brown amorphous powder, soluble in alkalis. The authors have also repeated and confirmed the work of Drost (*Annalen*, 1899, cccvii., 54) on the nitration products of ben*zis*ooxadiazole oxide. Both the mono- and the dinitroben*zis*ooxadiazole oxides, which are thus obtained, have strongly marked acid properties, turning Congo paper blue, and dissolving readily in aqueous alkalis.

*267. "*The Constitution of Aniline-black.*" (Part IV.). By Arthur George Green and William Johnson.

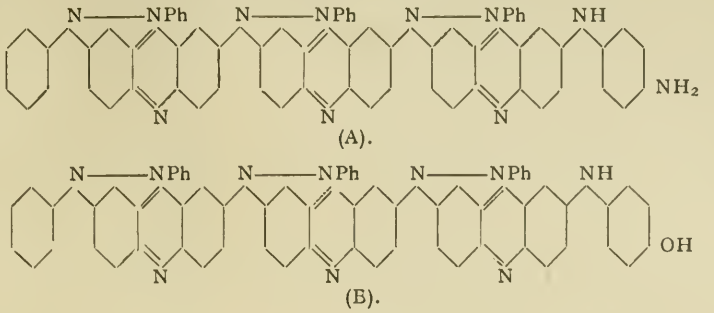
In further support of Green and Wolff's formula (A) for aniline-black base (chlorate oxidation) (*Proc.*, 1912, xxviii., 250) the following data have been obtained:—

1. On oxidation of aniline-black with lead peroxide and sulphuric acid a yield of benzoquinone is obtained, which corresponds with that required on the assumption that all the mono- and di-substituted benzene nuclei, but not the tri-substituted, will yield benzoquinone.

2. In presence of an excess of mineral acid aniline-black absorbs one molecule of sodium nitrite corresponding with the formation of a monodiazonium salt. Hence the terminal nitrogen atom forms an amino- and not an imino-group, and the chain must be an open one.

3. Titrations with hydrochloric acid have shown that aniline-black, in common with emeraldine and nigraniline, yields a non-hydrolysable dihydrochloride and a trihydrochloride, in which one molecule of hydrogen chloride is readily hydrolysed. Two of the nitrogen atoms are therefore strongly basic (quinonoid), whilst a third is weakly basic (amino-group). Leucoemeraldine, which contains no quinonoid nitrogen, does not give a stable hydrochloride.

4. Nigraniline does not condense with secondary aromatic amines, but only with primary amines.



(A).

(B).

5. The variety of aniline-black produced in solution by oxidation with chromic acid and known as "single bath black," or "bichromate black," has given results which indicate that it is the hydroxy analogue of ordinary aniline black (B). It is less basic than ordinary aniline-black, forming a non-hydrolysable dihydrochloride, but not a trihydrochloride. On oxidation it gives a yield of benzoquinone consistent with the formula given. In the above formulæ the colouring-matters are represented as anhydro-bases, but in both cases analysis indicates the presence of $1H_2O$ more, a fact explainable on the assumption that one phenylazonium group is present as an hydroxide or two such groups as an oxide.

Discussion.

Professor J. T. Hewitt agreed with Dr. Lowry in not liking an ortho-quinonoid formula for the free anhydrous bases of the safranine series. The linking of a quinquivalent nitrogen atom to a tervalent nitrogen atom attached to the same nucleus but in the meta-position seemed quite improbable, and when similar structures were given to *apo*safranone and its derivatives, the compounds were represented as betaines of a weakly acid phenolic group with a quaternary ammonium (powerfully basic) compound. This was at variance with the actual properties of *apo*safranone and its hydroxy-derivatives, since their basic properties were feeble. Arguments of a similar character might be urged against Professor Green's quaternary ammonium oxide formula for the hydrates of compounds of aniline-black type.

*268. "*The Constituents of Senna Leaves.*" By Frank Tutin.

Three specimens of senna leaves have been submitted to examination, namely—(I.) Tinnevelly senna leaves (*Cassia angustifolia*, Vahl; (II.) senna leaves from Lima, Peru, which were found to be botanically identical with the Tinnevelly leaves; and (III.) Alexandrian senna leaves (*Cassia acutifolia*, Delile).

The Tinnevelly leaves yielded, in addition to a small amount of essential oil, chlorophyll, and resinous products, the following definite substances—(i.) Salicylic acid; (ii.) rhein; (iii.) kæmpferol; (iv.) aloe emodin; (v.) *kaempferin*, $C_{27}H_{30}O_{16},6H_2O$ (m. p. 185—195°), a new glucoside of kaempferol; (vi.) a mixture of the glucosides of rhein and aloe-emodin; (vii.) the magnesium salt of an unidentified organic acid; (viii.) dextrose; (ix.) myricyl alcohol; (x.) a phytosterol; (xi.) a phytosterolin, $C_{33}H_{56}O_6$; (xii.) palmitic and stearic acids.

The Peruvian and Alexandrian senna leaves contained the above-mentioned compounds, with the exception of the magnesium salt, and, in addition, *iso*rhamnetin. The latter also occurred in the form of a glucoside.

The statements of Tschirch and Hiepe (*Arch. Pharm.*, 1900, ccxxxviii., 427), that senna leaves contain "senna-*iso*emodin," "sennachrysophanic acid" (chrysophanol), a "substance, $C_{14}H_{10}O_5$," and sennarhamnetin," cannot be confirmed, it having been ascertained that the anthraquinone derivatives present consist solely of rhein and aloe-emodin, whilst the flavone product is either kaempferol, or a mixture of the latter with *iso*rhamnetin.

*269. "*A Series of Mixtures of Nitro-compounds and Amines, which are Coloured in the Liquid State only.*" By Charles Kenneth Tinkler.

Certain nitro-compounds, when dissolved in fused diphenylamine and other amines, give strongly coloured solutions. The colour, however, entirely disappears on complete solidification of the mixture.

The most suitable substances for the demonstration of this phenomenon are mixtures of diphenylamine with one of the following nitro-compounds: *o*-, *m*-, and *p*-chloronitrobenzene, *m*- and *p*-nitrobenzaldehyde, *p*-bromonitrobenzene, tetranitromethane. By enclosing one of these mixtures between two test-tubes placed one inside the other, the phenomenon is well demonstrated. Thus, a mixture of diphenylamine and *p*-chloronitrobenzene, which is colourless at the ordinary temperature, acquires a reddish yellow colour when held in the hand, and loses this colour when the temperature falls.

A mixture of diphenylamine and *p* nitrobenzaldehyde shows a deep red colour at slightly above body temperature, returning to the colourless state on cooling.

A mixture of diphenylamine (solid) and tetranitromethane shows a dark brown coloration, but in a freezing mixture this colour is entirely removed.

From analogy to compounds of amines and nitro-derivatives, such as trinitrobenzene (Hepp, *Annalen*, 1882, ccxv., 344; Sudborough, *Trans.*, 1901, lxxix., 522; 1902, lxxxi., 587, &c.; Noelting and Sommerhoff, *Ber.*, 1906, xxxix., 76, and others), it is possible that the colour of these mixtures is due to the combination of the nitro-derivative and amine in the liquid state only. No direct evidence of compound formation has, however, so far been obtained from the various physico-chemical investigations which have been carried out.

Certain phenols and other substances may be substituted for the amine in the demonstration of the phenomenon, and the investigation is being extended in this direction.

Discussion.

In reply to the President, Dr. Tinkler said that the transient colorations produced were usually orange-red or red, although in the case of diphenylamine and tetranitromethane a very dark brown coloration was obtained. No transient blue or green colorations had been observed.

With reference to Dr. Senter's suggestion that the colour might be due to the presence of a small quantity of compound, Dr. Tinkler pointed out that, so far, no such indication had been obtained by the physico-chemical investigations which had been carried out with the mixtures. If, however, a compound was formed at all, it did not exist in the solid state, or the mixture would remain coloured on solidification and precipitation from solution.

270. "*A Study of some Organic Derivatives of Tin as regard their Relation to the Corresponding Silicon Compounds.* Part II. *Condensation Products of Dihydroxydibenzylstannane.*" By Thomas Alfred Smith and Frederic Stanley Kipping.

Organic derivatives of tin of the general formula

$SnR_2(OH)_2$ are unknown, but various oxides, SnR_2O, insoluble in all organic solvents, have been prepared.

The authors have attempted to obtain compounds of the dihydroxy-type in order to ascertain whether they are capable of existence, and, if so, whether they would give rise to open- and closed-chain condensation products analogous to those recently prepared from diphenylsilicanediol (Kipping, *Trans.*, 1912, ci., 2175).

The first product of the hydrolysis of dibenzyldichlorostannane with dilute potassium hydroxide solution seems to be the potassium derivative of the dihydroxy-compound; from the solution of this substance carbonic acid precipitates a solid, which is probably dibenzyldihydroxystannane, $Sn(CH_2Ph)_2(OH)_2$, but this compound is very unstable, and passes into a condensation product, which has probably the constitution $HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OH$.

This condensation product, unlike all the oxides, SnR_2O, is readily soluble in various organic solvents; when heated alone or in boiling bromobenzene solution, it passes into an insoluble oxide, which has probably the molecular formula $[Sn(CH_2Ph)_2O]_3$.

It may be concluded that all the insoluble oxides, $[SnR_2O]_n$, are condensation products of the unknown hydroxides; similarly, the ill-defined acids of the composition H_2SnO_3 are probably mixtures of even more complex condensation products of stannic hydroxide.

271. "*6'-Aminoquercetin.*" By EDWIN ROY WATSON.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1911, xxvii., 163).

272. "*Measurement of the Rate of Reaction by the Change of Volume in Solution.*" By ROBERT WRIGHT.

Although the alteration of volume resulting from chemical change has frequently been used to follow the course of a gaseous reaction—the formation of water vapour from its elements, for example—still it has seldom or never been applied to the case of reacting solutions. Such solution change is, as a rule, undoubtedly small, but even if it only amounts to about 0·2 per cent of the total volume, it gives a conveniet physical method for the determination of reaction velocities.

A few well-known reactions have been Investigated in this manner, but in some cases the change of volume is too small to be of service. For example, on heating an aqueous solution of pyrophosphoric acid, in a sealed tube for several hours at 100°, only a very slight change in the density of the solution takes place, and the same negative result is obtained by a similar heating of a solution of potassium cyanide. The hydrolysis of methyl acetate by sodium hydroxide is accompanied by considerable contraction in the reacting solution, but the change is inconveniently rapid, and the results are also masked by the rise of temperature which occurs.

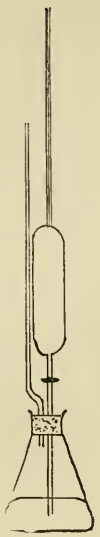
The rate of inversion of sucrose by an acid can readily be followed by means of the change of volume. A mixture of equal volumes of a 20 per cent solution of sucrose with 2N-hydrochloric acid showed the following densities before and after inversion :—

(*a*) After mixing..	1·0474	(*b*) After mixing..	1·0476
After 48 hours	1·0497	After 48 hours	1·0497

thus giving a contraction of volume equal to about 0·2 per cent.

In the determination of the velocity-constant, the apparatus shown was used. A pipette of about 50 cc. capacity has its upper tube of 1 mm. bore and 25 cm. long; the lower tube, which is fitted with a stopcock, passes through a rubber cork, and reaches almost to the bottom of a 150 cc. flask; a side-tube open to the air also passes through the rubber stopper.

The pipette is first charged with a 20 per cent solution of sucrose, which is run into the flask, and a few grains of mercuric iodide are added as preservative; the pipette is then rinsed out and charged with 2N-hydrochloric acid, and the stopcock being closed, it is placed in position in the flask. The apparatus is now immersed in a thermostat at 25°, and allowed to attain the temperature of the bath; the tap is opened, and by applying suction to the side-tube the acid is drawn into the flask; the mixture is well stirred by drawing air through it, and is then forced back into the pipette until it stands at a level of a few cm. from the top of the capillary tube. It is absolutely essential to have some of the mercuric iodide carried into the pipette along with the solution, otherwise fermentation of the sugar will cause minute bubbles of gas to be formed; for the same reason it is necessary to steam out the apparatus before use. The pipette being charged, the tap is closed, and the level of the liquid in the tube read; this gives the zero reading. The fall of the liquid is now read at definite intervals, and a final reading is taken after forty-eight hours, when the total fall should befrom 10 to 20 cm. The velocity constant may now be calculated in a manner quite analogous to that used with the polarimeter.



In the following example a = final distance between the level of the liquid and the top of the tube, and x_1 and x_2 are the distances corresponding with the times t_1 and t_2. Then k, the velocity-constant, is given by :—

$$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}.$$

Time in hrs.	Time in mins.	Reading from top. Mm.	K.
0	0	15·0	
0	15	23·0	0·01177
0	30	29·5	0·00483
0	45	35·5	0·00479
1	0	41·3	0·00498
1	30	51·5	0·00489
2	0	60·0	0·00470
2	30	67·0	0·00450
3	0	73·5	0·00473
48	0	a = 116·0	

Leaving out of consideration the first value of K which is affected by the rise of temperature at the beginning of the reaction, it is seen that the numbers agree to within about 5 per cent of each other, the true value given by the polarimeter being 0·00470.

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut).

273. "*Amalgams containing Silver and Tin.*" By WILLIAM ARTHUR KNIGHT and REGINALD ARTHUR JOYNER.

It was again shown that the ageing of alloys of silver and tin is not due to superficial oxidation. A bar of alloy does not age appreciably even after fifteen days at 115°, whereas filings of the same bar are aged after half-an-hour at 100°. Hence it is concluded that ageing is not due to any uncatalysed polymorphic change in the Ag_3Sn contained in the alloy. It was also proved that ageing is not due to sorption of oxygen by the filings. A further hypothesis to be tested is that it may be due to catalytic action of the iron or products of iron introduced during the filing.

The equilibrium of the metals silver, tin, and mercury at temperatures of 63°, 90°, 166°, and 214° has also been studied. The liquidus has been completely determined at these temperatures, and consists of a line roughly parallel to the Sn-Hg side of the equilateral triangle. At 63° this line only extends about one tenth of the distance across the diagram, whereas at 214° it stretches nearly the whole way across. The solidus has not, as yet, been determined

accurately, but there are good reasons for considering that, commencing at the point Ag_3Hg_4, it extends across the diagram roughly in the direction of Ag_3Sn. It has been proved that the substances represented by points on the solidus must be solid solutions.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology and Analysis of Oils, Fats, and Waxes. By Dr. J. Lewkowitsch, M.A., F.I.C. Fifth Edition. Volume I. London: Macmillan and Co., Ltd. 1913.

Some new analytical methods are described in the fifth edition of this treatise, and a considerable amount of new material has been added to it, so that its bulk has had to be much increased. The first volume deals with the chemistry and analysis of the oils, fats, and waxes. In the early chapters the classification and the physical and chemical properties are discussed, and the saponification of fats and waxes and the chemical nature of their constituents. Physical and chemical methods of examining them are also described, quantitative preceding qualitative methods, and the examination of fixed fatty acids and of unsaponifiable matter is treated in the last chapters. The second and third volumes are promised quite shortly, and with them the complete index will be issued.

Digitalis Assay. By W. Harrison Martindale, Ph.D. (Marburg), F.C.S. London: H. K. Lewis. 1913.

The colorimetric method of assaying digitalis described by the author of this book has the advantages of being easy to perform and requiring only simple apparatus. The whole operation takes about three hours, and when carried out by an investigator of average skill it is claimed that, although it cannot be relied upon for absolute accuracy it will show, without leaving any room for doubt, whether a given specimen is exceptionally weak or strong. The author strongly deprecates the use of animals for the routine work of testing, and contends that for all ordinary purposes his method is as valuable as the physiological method. The book contains short abstracts of most of the work that has been published on digitalis assaying, and besides describing in full detail the perfected method of carrying out his test the author gives some account of the preliminary experiments from which it was evolved. He has also something to say about the importance of the standardisation of the drug and about the ideal conditions for the growth of the plant. From the results of his work he has formed the opinion that any method of standardisation based upon the content of Digitoxin cannot be regarded as really satisfactory, since the water-soluble constituents are not entirely without therapeutic action, and digitoxin itself appears to be not quite insoluble in water.

A Text Book of Quantitative Chemical Analysis. By Alexander Charles Cumming, D.Sc. and Sydney Alexander Kay, D.Sc. London: Gurney and Jackson. 1913.

This book on quantitative analysis will provide the student with a good training in the subject, and in consequence of its comparatively wide scope it will be found specially suitable for the use of those who cannot give very much time to practical chemistry, and who nevertheless require a good general knowledge of all the most important branches of analytical work. It begins with volumetric analysis, which in the author's opinion has more educative value than gravimetric work. Electrolytic methods are nclud ed and some colorimetric estimations, as well as gas analysis and easy organic combustions. The treatmen of some fairly simple alloys and ores is discussed, and a good feature is the prefacing of each detailed description by a short outline of the method to be employed, so that the student is given no excuse for not knowing exactly what he is driving at. In one section of the book the systematic quantitative analysis of all the common metals and radicles, arranged alphabetically, is given, including both separations and determinations, and this section will be very useful for reference and revision.

Pyrites in Canada. By Alfred W. G. Wilson, Ph.D Ottawa: Government Printing Bureau. 1912.

The extension of the manufacturing industries in Canada, and in particular of the sulphite pulp process, has led to many enquiries as to the country's supplies of pyrites, for which there is a large and growing demand. The writer of this bulletin has endeavoured to bring together all that is known about the occurrence, dressing, and uses of pyrites in Canada, and gives practical information for the benefit of both the producer and the consumer. Details of the localities in which the ore has been found are included, and accounts are given of methods of working and of the different types of furnaces used in roasting it. The manufacture and uses of sulphuric acid are also described, and a chapter on the Paper Manufacturing Industry deals with the use of pyrites as a substitute for sulphur in the sulphite fibre industry.

The Flash Point of Oils. By Irving C. Allen and A. S. Crossfield. Washington: Government Printing Office. 1913.

This Technical Paper, issued by the Bureau of Mines, contains short descriptions of different types of instruments for determining the flash point of oils, and also a complete bibliography of methods and apparatus. The authors discuss at length the various factors which have to be taken into consideration in the determination, and recommend as the most reliable instruments the Abel-Pensky and the Pensky-Martens testers. The construction and manipulation of both of these are described in some detail, and the use of simple testers, which can be employed when great accuracy is not required, is also shortly treated.

Our Artesian Waters. By R. S. Symmonds. Sydney: W. A. Gullick. 1912.

The author of this bulletin on the Artesian water supply of Australia believes that the diminution in the flow and pressure of certain bores is due not to lack of water, but to leakage and the corrosion of casings, and in the bulletin he brings forward the evidence upon which he bases this important conclusion. He also discusses the analysis of the waters from different localities and the injurious effects of the alkaline salts in them. Some very interesting culture experiments are described, and the striking results which have been obtained by treating the soil with dilute nitric acid to neutralise the alkalinity are illustrated.

The Scientists' Reference Book and Diary for 1914. Manchester: James Woolley, Sons, and Co., Ltd.

This is a very convenient sized pocket-book, well bound in morroco leather, with a good plain diary for the year. There is ample space for memoranda, &c., card and postage stamp pockets, together with a reference book of 132 pages, printed on thin paper containing the usual budget of information that is continually needed by the professional man (or woman). A very compact review of "Science in 1913," by E. S. Grew, M.A., is included, in which the various advances that have been made during the year are briefly noted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

TE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 18, November 3, 1913.

Alkylation of β- and γ-Methylcyclohexanones by means of Sodamide.—A. Haller.—When the β- and γ-methylcyclohexanones are subjected to methylation or ethylation by means of a halogen compound in presence of sodamide, the ketone always condenses with itself besides undergoing the desired alkylation. The condensation is more marked the further the methyl group is from the ketonic group; it attains its maximum with cyclohexanone, the non-methylated ketone. Other things being equal the condensations of the ketones with themselves are more marked in ethylation than in methylation. The yield of alkylated ketone is greater the nearer the original methyl is to the ketone group.

Distillation of Oil under Reduced Pressure.—Amé Pictet and Maurice Bouvier.—The authors have distilled a fatty oil from Montrambert (Loire) under a reduced pressure at as low a temperature as possible, and have investigated the products, which separate into two layers: an aqueous solution (about 1·5 per cent by weight of the oil) possessing an acid reaction, and not containing ammonia, and a special tar (about 4 per cent). This tar, which the authors call "vacuum tar," differs essentially from ordinary tar in properties and composition. It is fairly fluid, light brown in colour, and lighter than water. It contains very little aromatic substance or none at all, and all its properties resemble those of petroleum, especially Caucasian petroleum. When it is subjected to a second distillation the principal constituents of ordinary tar are obtained, and hence "vacuum tar" is an intermediate product of the distillation of oil at the ordinary pressure, and at a higher temperature it undergoes decomposition into the products which constitute ordinary tar.

6-Aminopiperonal.—Aug. Rilliet and L. Kreitmann.—6-Aminopiperonal can be prepared by the reduction of 6-nitropiperonal by means of sodium sulphide, but it is necessary to use an indirect method by which the aldehyde group is protected against a secondary action of the sulphide and also against a condensation with the amine group formed. For this purpose 6-nitropiperonal is condensed with paratoluidine, and the aminopiperonylideneparatoluidine obtained is reduced with sodium sulphide and then hydrolysed by boiling with water made slightly alkaline.

Atti della Reale Accademia dei Lincei. Vol. xxii. [ii.], No. 5, 1913.

Decomposition of Racemic Amino Acids by means of Active Acids.—Amedeo Colombano and Giuseppe Sanna.—The authors have endeavoured to split up glycocoll and α-alanine into their optical isomers by means of *d*-camphosulphonic acid and *d*-bromocamphosulphonic acids. In both cases the attempts always failed, although the experimental conditions were varied within wide limits.

Vol. xxii. [ii.], No. 6, 1913.

Decomposition of α-Alanine into its Optical Antipodes by means of Active Acids.—Amedeo Colombano and Ginseppe Sanna.—α-Alanine can be split up into its optical antipodes by means of such active acids as campho or bromocampho-sulphonic acids, if it is first esterified by Fischer's method. The esters are substances which are readily characterised by their boiling-points, solubility, and melting-point of their picrates.

MISCELLANEOUS.

Anglo-American Exposition, London (May—October), 1914.—The Committee of the Chemical Industries Section of the Anglo-American Exposition of 1914 is hoping to arrange the most extensive collection of exhibits ever brought together and to make it worthy of the British Empire, and undoubtedly the exhibits from the United States will be of the highest order. The Exposition will give manufacturers an unique opportunity of bringing British chemical industries to the notice of visitors from all parts of the world. A very influential committee has been appointed, and the following are the sub-sections in which the exhibits will be arranged:—*Sub-section* I.—Apparatus and Machinery common to Chemical Industries. *Sub-section* II.—Mineral Acids, Alkalis, and all kinds of Salts. *Sub-section* III.—Materials and Processes connected with Heating and Lighting. *Sub-section* IV.—Explosives of all kinds and Matches. *Sub-section* V.—Sugar, Starch, and Alcoholic Products. *Sub-section* VI.—Appliances and Processes for the Treatment of Sewage, &c. *Sub-section* VII. Dyes, Pigments, &c, *Sub-section* VIII.—Paper and Artificial Textile Materials. *Sub-section* IX.—Leather, Rubber, &c. *Sub-section* X,—Drugs and Pharmaceutical Products, &c. *Sub-section* XI.—Essential Oils and Perfumes. *Sub-section* XII. Tobacco and Snuff.

The National Physical Laboratory. British Radium Standard.—By resolution of the International Standards Committee in March, 1912, a preparation of 21·99 mgrms. of pure radium chloride, prepared by Mdme. Curie, was declared to be the International Standard, and deposited at the Bureau International des Poids et Mesures at Sèrves. The National Physical Laboratory, Teddington, Middlesex, is in possession of the British Radium Standard, which has been certified by the International Committee after comparison with the International Standard. The Laboratory is prepared to undertake the standardisation of radium and mesothorium preparations by comparison with the Standard. For the present the Laboratory will confine itself to the testing of specimens which permit the use of methods depending on the measurement of the penetrating γ-rays. This method requires that the preparation shall have been completely closed in a containing vessel for at least six weeks before the test, as until that time has elapsed the intensity of the γ-rays is not proportional to the quantity of radium present. If the specimen, after a test lasting ten days or more, proves to be in radio-active equilibrium a certificate will be granted by the Laboratory, giving the date of test and the equivalent content of metallic radium within the limits of accuracy of the measurement, provided this content is in excess of 1 mgrm. It is requested that when possible the specimen shall be enclosed in a thin-walled vessel of small dimensions. The scale of fees is as follows:—Samples up to and including 10 mgrms. metallic radium, £3 3s.; more than 10 mgrms. and up to and including 40 mgrms., £4 14s. 6d.; more than 40 mgrms. and up to and including 80 mgrms., £7 7s. In the case of a sample containing less than 1 mgrm. of metallic radium a certificate will not ordinarily be issued; its place will be taken by a statement to the effect that the sample does not contain more than some specified amount of the metal. A person wishing to send radium for test must advise the Laboratory of his intention at least one day previous to sending the specimen. The letter of advice should state approximately the value of the specimen and the method by which it is being sent. All communications and specimens should be addressed to The Director, The National Physical Laboratory, Teddington, Middlesex, and all packages containing specimens should be clearly marked "R Department."

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 30th. } Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner, D.Sc., F.R.S.
THURSDAY, Jan. 1st. }
SATURDAY, „ 3rd. }

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